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Water-Related Environmental Fate of 129 Priority Pollutants

Volume II

Halogenated Aliphatic Hydrocarbons
Halogenated Ethers
Monocyclic Aromatics
Phthalate Esters
Polycyclic Aromatic Hydrocarbons
Nitrosamines
Miscellaneous Compounds

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16. ABSTRACT

This report is a literature search and summary of relevant data for the individual fate processes (hydrolysis, biodegradation, photolysis, etc.) which might be expected to occur if a pollutant were introduced into an aquatic system. The report is organized into 101 individual chapters for pollutants or small groups of pollutants, and four introductory chapters. Each chapter has its own references so the chapters can be used independently.

The approach taken by this report is to summarize data on the individual processes which might be important in describing the transport and fate of pollutants introduced at low concentrations (e.g., ppm or less) into aquatic environments. If transport processes will result in significant pollutant transfer to another medium (e.g., air, sediments), data are included where available to describe what happens to the pollutant in the medium to which the pollutant was transferred.

A list of the literature covered in the search is included.

Results of the literature search are that a significant amount of information on most pollutants was found, but that the information was more useful in making qualitative judgements about the pollutant transport and fate than for making quantitative predictions of concentrations in the environment. Availability of rate constants useful in mathematical fate models was limited.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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Pollutants	Toluenes		07B, 07C, 07D
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Transport	Pesticides	Environmental Fate	97R
Water Pollution	Metals		57H
Halogenated Hydrocarbons	Esters		68D, 68E, 68A
Organic Nitrogen Compounds	Nitriles		99E
Aromatic Polycyclic Hydrocarbons	Ethers		

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WATER-RELATED ENVIRONMENTAL FATE OF 129 PRIORITY POLLUTANTS

Volume II:

Halogenated Aliphatic Hydrocarbons, Halogenated Ethers, Monocyclic Aromatics, Phthalate Esters, Polycyclic Aromatic Hydrocarbons, Nitrosamines, and Miscellaneous Compounds

by

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B

FOREWORD

Effective regulatory action for toxic chemicals requires an understanding of the human and environmental risks associated with the manufacture, use, and disposal of the chemical. The assessment of risk requires a scientific judgment about the probability of harm to the environment resulting from known or potential environmental concentrations. Environmental concentrations are a function of (1) the amount and form of the chemical released into the environment, (2) the geographic area, (3) prior accumulation, (4) time of measurement, and (5) the behavior of the chemical in the environment. The behavior, or fate and transport characteristics, of toxic pollutants in the environment depends on a variety of chemical, physical, and biological processes (e.g., photolysis, hydrolysis, volatilization, sorption, biodegradation, biotransformation). Evaluating these processes for specific compounds and placing each interaction into environmental perspective is the basic goal of this report.

This two-volume report is a comprehensive review of the water-related environmental fate and transport literature available for 129 chemical compounds and elements, sometimes referred to as the 129 priority pollutants.

Michael W. Slimak, Chief
Exposure Assessment Section
Water Quality Analysis Branch
Monitoring and Data Support Division (WH-553)
Office of Water Planning and Standards

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SECTION V: HALOGENATED ALIPHATIC HYDROCARBONS

Chapters 38-63

38. CHLOROMETHANE (METHYL CHLORIDE)

38.1 Statement of Probable Fate

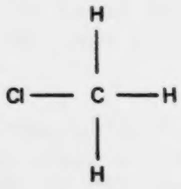
Volatilization is the major transport process for removal of chloromethane from aquatic systems. Once in the troposphere chloromethane is attacked by hydroxyl radicals with the subsequent formation of formyl chloride as the principal initial product. Any unreacted chloromethane reaching the stratosphere will undergo photodissociation.

Based on the information currently reviewed, it appears that oxidation, hydrolysis, and biodegradation are not important fate processes of chloromethane in the aquatic environment. No information was found indicating that adsorption and bioaccumulation are important environmental transport processes for chloromethane.

38.2 Identification

Chloromethane is known to be ubiquitous in the environment. It enters the environment from natural as well as anthropogenic sources, and has been detected in finished drinking water (Environmental Protection Agency 1975), in seawater (Lovelock 1975; Singh *et al*. 1978), and in the troposphere (Singh *et al*. 1978).

The chemical structure of chloromethane is shown below.



Chloromethane

CAS NO. 74-87-3
TSL NO. PA 63000

Alternate Names

Methyl chloride
Monochloromethane

38.3 Physical Properties

The general physical properties of chloromethane are as follows.

Molecular weight (Weast 1977)	50.59
Melting point (Weast 1977)	-97.73°C

Boiling point at 760 torr (Weast 1977)	-24.2°C
Vapor Pressure at 20°C (McConnell *et al*. 1975)	3765 torr
Solubility in water at 20°C (McConnell *et al*. 1975)	6450 to 7250 mg/l*
Log octanol/water partition coefficient (Hansch *et al*. 1975)	0.91

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*Several values for solubility of chloromethane in water at 20°C were found in the literature. These values range from 6450 mg/l (Dean 1973) to 7250 mg/l (Pearson and McConnell 1975).

38.4 Summary of Fate Data

38.4.1 Photolysis

No information was found pertaining to the rate of photolysis of chloromethane in the aqueous environment under ambient conditions. Dilling *et al*. (1975) studied the decomposition rates of dichloromethane and trichloromethane, compounds structurally similar to chloromethane. At a concentration of one ppm in water, in aerated sealed tubes, Dilling *et al*. (1975) found no significant difference between decomposition rates of these compounds in tubes exposed to sunlight and those kept in dark over periods of 6 and 12 months.

Due to the high vapor pressure of chloromethane, volatilization to the atmosphere is believed to be quite rapid. Inasmuch as the ozone layer above the earth absorbs all wavelengths of light below about 290 nm (Koller 1965) and chloromethane does not absorb light at wavelengths above 290 nm, appreciable photodissociation below the ozone layer (in the troposphere) would not be expected to occur. Chloromethane in the troposphere is attacked, via hydrogen abstraction, by hydroxyl radicals (Hanst 1978; Spence *et al*. 1976). The rates are such that this photooxidation reaction appears to be the predominant fate process for chloromethane.

The wavelength region in which most photodissociation in the stratosphere occurs is from about 180 to 240 nm (Robbins 1976). It has been experimentally determined that chloromethane undergoes light absorption from 174 to about 200 nm (Robbins 1976). As a result, any unreacted chloromethane reaching the stratosphere would be expected to undergo significant photodissociation.

38.4.2 Oxidation

No information was found pertaining specifically to the oxidation of chloromethane in the aqueous environment. Dilling et al. (1975) conducted aqueous reactivity experiments on $CHCl_2$ and $CHCl_3$ (compounds structurally similar to chloromethane) in which there was a large excess of dissolved oxygen compared to the total amount of dichloromethane and trichloromethane. The air space above the solution in the closed system contained approximately 90 times as much oxygen as was present in the saturated solution. Since the observed rates of decomposition were much smaller than rates of volatilization determined by the same authors for chloromethane, dichloromethane and trichloromethane, and since most of the decomposition was attributed to ionic hydrolysis rather than oxidation, it is concluded that oxidation in the aqueous system is not an important process for chloromethane.

Due to the high vapor pressure of chloromethane, volatilization to the atmosphere should be quite rapid, and once in the troposphere, chloromethane is attacked by hydroxyl radicals via the mechanism of hydrogen abstraction (Hanst 1978; Spence et al. 1976). The bimolecular rate constant for reaction of chloromethane with ·OH is reported by Cox et al. (1976) to be $8.5 \times 10^{-14} cm^3 sec^{-1}$, corresponding to a lifetime (time for reduction to 1/e) of 0.37 years. This agrees reasonably well with the rate constant of $1.69 \times 10^{-12} \exp(-1066/T)\ cm^3 sec^{-1}$, or $4.7 \times 10^{-14} cm^3 sec^{-1}$ at 25°C, reported by Yung et al. (1975) and reflecting a lifetime, described as an upper limit, of 0.89 years.

The principal initial product of this photooxidation reaction is reported to be formyl chloride (HCOCl), with hydrogen peroxide (H_2O_2), carbon monoxide (CO) and hydrogen chloride (HCl) being formed in smaller quantities (Spence et al. 1976). Formyl chloride is readily hydrolyzed to HCl and CO (Morrison and Boyd 1973).

With the assumption of 30 years as the troposphere-to-stratosphere turnover time (time for all but 1/e of tropospheric air to diffuse into the stratosphere), the 0.37 year tropospheric lifetime for chloromethane of Cox et al. (1976) corresponds to about one percent of tropospheric chloromethane eventually reaching the stratosphere.

38.4.3 Hydrolysis

A hydrolytic half-life of 417 days (1.14 years) has been reported for chloromethane at pH 7 and 25°C (Mabey and Mill 1978; Radding et al. 1977). This corresponds to a first-order rate constant for hydrolysis of chloromethane of $1.9 \times 10^{-8} sec^{-1}$ (Mabey and Mill 1978; Radding et al. 1977). The solvolysis of chloromethane in water at 20°C is reported to proceed at a pseudo-first order rate of $8.9 \times 10^{-9} sec^{-1}$ corresponding to a half-life of 2.5 years (Zafirion 1975); however, no measurement of pH was given. Due to the high vapor pressure and low boiling point of this compound, it is expected that most of the chloromethane present in water will be transported to the atmosphere more rapidly than it will react with water.

38.4.4 Volatilization

Dilling et al. (1975) estimated the experimental half-life for volatilization of chloromethane originally present at 1 mg/l to be 27 minutes when stirred at 200 rpm in water at approximately 25°C in an open container. Removal of 90 percent of the chloromethane under the same conditions required 91 minutes. For chloroaliphatics in general, stirring speed was found to have a marked effect on volatilization rate. With no stirring except 15 seconds every five minutes the time required for 50 percent depletion of compounds such as trichloromethane, trichloroethene, and 1,1,1-trichloroethane, which are structurally similar to chloromethane, was greater than 90 minutes, or on the order of three times greater than the stirred case for these compounds.

Evaporation appears to be the major pathway by which chloromethane is transported from the water. Dilling et al. (1975) are careful to point out the difficulties encountered in extrapolating their laboratory results to real-world conditions, where the concentration of the organic solute would probably be very much less than 1 mg/l and where surface and bulk agitation would be highly variable. Although the data appear to be valid on a relative basis (i.e., correctly illustrating the relative rates of volatilization of chlorinated aliphatics), they cannot be used as absolute measures of volatilization rates from natural waters. For the purposes of this document, the data are used as rough-order-of-magnitude indications of the importance of volatilization relative to other transport and fate processes, with the strong effects of agitation considered. The validity of this application has not been established.

A subsequent study by Dilling (1977) used the same experimental conditions as in the 1975 study, and an average half-life for volatilization of 27.6 minutes for 1 mg/l chloromethane was obtained. The purpose of this subsequent study was to use the experimental data obtained to test two theoretical models formulated to predict evaporation rates of slightly soluble organic compounds from water. Dilling (1977) found that the theoretical model of Mackay and Wolkoff (1973) failed to predict evaporative half-lives, but that the model of Mackay and Leinonen (1975) using parameters from Liss and Slater (1974) correlated well with experimental results. For example, the evaporative half-life for chloromethane obtained experimentally by Dilling (1977) was approximately 28 minutes as compared to 14.9 minutes predicted by the Mackay and Leinonen (1975) model and 0.599 minutes predicted by the Mackay and Wolkoff (1973) model.

Dilling (1977), however, comments that the apparent numerical agreement between his data and the values predicted by the Mackay and Leinonen (1975) model may be fortuitous. Estimates of volatilization rates based on the Mackay and Leinonen (1975) model depend primarily on liquid-gas phase exchange rate constants, whereas the experimental model of Dilling et al. (1975) and Dilling (1977) is controlled by the rate of stirring and the wind velocity across the surface of the water.

Pearson and McConnell (1975) suggest that the presence of chloromethane in ambient waters is due to absorption of chloroorganics from the atmosphere by water. This absorption is thought to occur most effectively when the atmosphere is scrubbed during the precipitation process. Aerial transport of these chloroorganics, as well, is postulated by Pearson and McConnell (1975) to play a major role in the wide distribution of these compounds and accounts for their presence in upland waters.

38.4.5 Sorption

No data on sorption processes specifically involving chloromethane were found. The importance of sorption relative to other transport and fate processes is controlled by the partitioning of the subject chemical between the particulate, aqueous and air phases. In the case of chloromethane, its high vapor pressure, only moderately low aqueous solubility and relatively low (for chlorinated aliphatics) octanol/water partition coefficient seem to indicate that this compound would partition primarily into the air and water compartments rather than into sediments and suspended particulates.

38.4.6 Bioaccumulation

According to Kopperman et al. (1976) not all organochlorine compounds bioaccumulate to high levels. The data suggest that polar compounds are more easily biodegraded, whereas non-polar, highly lipophilic compounds accumulate. Neely et al. (1974) have shown that bioaccumulation is directly related to the octanol/water partition coefficient (P) of the compound. The log octanol/water partition coefficient (lop P) of chloromethane is 0.91 (Hansch et al. 1975), indicating that chloromethane is not very lipophilic. As a result, chloromethane would not be expected to exhibit a significant tendency to bioaccumulate in organisms.

38.4.7 Biotransformation and Biodegradation

No information was found pertaining specifically to the biodegradation of chloromethane. If the partitioning of chloromethane in the aqueous environment favors the air and aqueous compartments over particulates (including biota), as postulated above in the section on sorption, then biodegradation would not be expected to be an important fate process for this chemical.

38.5 Data Summary

Table 38-1 summarizes the aquatic fate data found above. Oxidation rates are photooxidation rates and refer to the rate of reaction of chloromethane with hydroxyl radicals in the troposphere.

The predominant fate of chloromethane is a result of the high vapor pressure of this compound which causes it to volatilize rapidly into the atmosphere. Once in the troposphere, chloromethane is attacked by hydroxyl radicals resulting in the subsequent formation of formyl chloride as the principal product.

Table 38-1

Summary of Aquatic Fate of Chloromethane

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Probably not significant in aquatic systems.	-	-	Medium
Oxidation[c]	The predominant fate of this compound is attack by hydroxyl radicals in the troposphere.	$8.5 \times 10^{-14} cm^3 sec^{-1}$	0.37 years[a]	High
Hydrolysis	Is probably not a significant fate.	$1.9 \times 10^{-8} sec^{-1}$	417 days	High
Volatilization	Primary transport process from the aquatic environment.	-	27 minutes[b]	Medium
Sorption	Probably not significant.	-	-	Medium
Bioaccumulation	Probably does not significantly bioaccumulate in organisms.	-	-	Medium
Biotransformation/ Biodegradation	Probably not important.	-	-	Medium

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a. Reported as a lifetime (time for reduction to 1/e of original concentration) of 0.37 years.

b. Half-lives are on the order of several minutes to a few hours, depending on the degree of agitation. The value reported was determined in a stirred container.

c. The predominant environmental process which is thought to determine the fate of the compound.

38.6 Literature Cited

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39. DICHLOROMETHANE (METHYLENE CHLORIDE)

39.1 Statement of Probable Fate

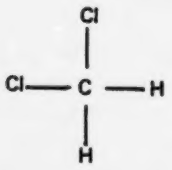
Volatilization is the major transport process for removal of dichloromethane from aquatic systems. Once in the troposphere, dichloromethane is attacked by hydroxyl radicals with the subsequent formation of carbon dioxide, carbon monoxide, and phosgene as principal, initial products. Any unreacted dichloromethane which reaches the stratosphere will undergo photodissociation.

Based on the information reviewed, it appears that neither oxidation nor hydrolysis is an important fate process of dichloromethane in the aquatic environment. No information was found to indicate that either adsorption or bioaccumulation is an important transport process for dichloromethane.

39.2 Identification

Dichloromethane (methylene chloride) has been detected in finished drinking water (Environmental Protection Agency 1975) and in the troposphere (Singh *et al*. 1978).

The chemical structure of dichloromethane is shown below.



$$\begin{matrix} & \mathrm{Cl} & \\ & | & \\ \mathrm{Cl} - & \mathrm{C} & - \mathrm{H} \\ & | & \\ & \mathrm{H} & \end{matrix}$$

Dichloromethane

Alternate Names

Methylene chloride
Methylene dichloride
Methane dichloride
Methylene bichloride

CAS NO. 75-09-2
TSL NO. PA 80500

39.3 Physical Properties

The general physical properties of dichloromethane are as follows.

Molecular weight (Weast 1977)	84.94
Melting point (Weast 1977)	-95°C

Boiling point at 760 torr (Weast 1977)	39.75°C
Vapor pressure at 20°C (Pearson and McConnell 1975)	362.4 torr
Solubility in water at 25°C	13,200 to 20,000 mg/l*
Log octonal/water partition coefficient (Hansch *et al*. 1975)	1.25

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*Several values for solubility of dichloromethane in water at 20°C were found in the literature. These values range from 13,200 mg/l (Pearson and McConnell 1975) to 20,000 mg/l (Dean 1973)

39.4 Summary of Fate Data

39.4.1 Photolysis

Dilling *et al*. (1975) studied the rate of decomposition of dichloromethane at a 1 mg/l concentration in water in aerated sealed tubes and found no significant difference between the half-life of dichloromethane in tubes exposed to sunlight and those kept in darkness over a period of one year. This result indicates that photochemical reactions in aqueous media are probably not important for dichloromethane.

Photodissociation in the aquatic environment would not be expected to occur for dichloromethane since this compound has no chromophores which absorb in the visible or near ultraviolet region of the electromagnetic spectrum (Jaffé and Orchin 1962). An experiment was conducted by Dilling *et al*. (1976) which simulated environmental exposure to sunlight (wavelengths > 290 nm and a temperature of 27 ± 1°C). Experimental results showed that dichloromethane decomposed at a rather slow rate under tropospheric conditions with either NO or NO_2 present; the estimated photodecomposition half-life was greater than 250 hours.

39.4.2 Oxidation

Little information pertaining to the oxidation of dichloromethane in the aqueous environment under ambient conditions was found. Dilling *et al*. (1975) conducted aqueous reactivity experiments in which there was a large excess of dissolved oxygen compared to the total amount of dichloromethane. The air space above the solution in the closed system contained approximately 90 times as much oxygen as was present in the saturated solution. The observed rate of disappearance, which was attributed primarily to ionic hydrolysis rather than oxidation, was much lower than rates of volatilization reported for dischloromethane by the same authors. From these results, it is concluded that oxidation in the aqueous phase probably is not important for dichloromethane. Due to the high vapor pressure of dichloromethane, volatilization to the atmosphere is quite rapid. Once in the troposphere, the compound is attacked by hydroxyl radicals (OH·) via hydrogen abstraction (Hanst 1978; Spence 1976). The rate of this reaction is reported to be 1.04 x $10^{-13}cm^3sec^{-1}$ corresponding to a lifetime of 0.30 years (Cox et al. 1976). The principal product of this photooxidation reaction is reported to be carbon dioxide (CO_2), with carbon monoxide (CO) and some phosgene ($COCl_2$) being formed in smaller quantities (Spence et al. 1976). Phosgene is readily hydrolyzed to HCl and CO_2 (Morrison and Boyd (1973).

For a troposphere-to-stratosphere turnover time (time for all but 1/e of tropospheric air to diffuse into the stratosphere) of 30 years, a 0.30 year tropospheric life time (Cox et al. 1976) would result in about one percent of tropospheric dichloromethane reaching the stratosphere. Once in the stratosphere, dichloromethane would be expected to undergo phodissociation resulting from interaction with high energy ultraviolet radiation.

39.4.3 Hydrolysis

A maximum hydrolytic half-life of 704 years, extrapolated from experimental data obtained at 100-150°C, has been reported for dichloromethane at pH 7 and 25°C (Radding et al. 1977). This corresponds to a reported first-order rate constant for hydrolysis of dichloromethane of 3.2 x $10^{-11}sec^{-1}$. The validity of the extrapolation method used by Radding et al. (1977) has not been established. The data above are not at all in agreement with the results of the aqueous reactivity experiments of Dilling et al. (1975), described previously, which indicated a (first-order) rate of disappearance at 25°C of 0.039 $months^{-1}$, corresponding to a half-life of approximately 18 months for dichloromethane. The authors attributed most of the effect noted to ionic hydrolysis, although oxidation and vapor-phase hydrolysis were also possible in the experimental system used. At best, the results of Dilling et al. can be interpreted as a maximum rate (minimum half-life) for hydrolysis of dichloromethane in aqueous systems.

A study by Fells and Moelwyn-Hughes (1958) investigated the behavior of dichloromethane when hydrolyzed in water under acidic and basic conditions in the temperature range 353-423°K (80-150°C). The hydrolysis of dichloromethane in acidic solution follows a simple, first-order rate law. The acid hydrolysis of dichloromethane at 373.16°K (100°C) is reported to proceed at a rate of 5.77 ± 0.05 sec^{-1}, which corresponds to a measured half-life period of 19,800 minutes (13.75 days). Experimentally, it was found that hydrochloric acid and formaldehyde are produced in equivalent concentrations from the beginning of the reaction. The reaction takes place in two stages, and can be represented as follows:

$$\begin{array}{ll} (1) & CH_2Cl_2 + H_2O \longrightarrow CH_2Cl(OH) + HCl \\ (2) & CH_2Cl(OH) \longrightarrow CH_2O + HCl \end{array}$$

The kinetics of the hydrolysis of dichloromethane in alkaline solution were examined by Fells and Moelwyn-Hughes (1958) with potassium hydroxide as the catalytic agent. Reaction between dichloromethane and hydroxide ion in aqueous solution is not a simple second-order reaction. Reaction with the solvent (water) occurs, and, in addition, the formaldehyde being formed reacts with the potassium hydroxide, giving methyl alcohol and formate ion as products (Cannizzaro reaction). The reaction can be represented as follows:

$$\begin{array}{ll} (1) & CH_2Cl_2 + HOH \xrightarrow{k^1} CH_2O + 2\ H^+ + 2\ Cl^- \\ (2) & CH_2Cl_2 + 2\ OH^- \xrightarrow{k^2} CH_2O + 2\ Cl^- + H_2O \\ (3) & 2\ CH_2O + OH^- \longrightarrow HCO_2{}^- + CH_3OH \\ & \text{(Cannizzaro Reaction)} \end{array}$$

The alkaline hydrolysis of dichloromethane at 373.16° K (100°C) from reaction (2) above is reported to be 1.61×10^{-4} l $mole^{-1} sec^{-1}$.

39.4.4 Volatilization

Dilling et al. (1975) estimated the experimental half-life for volatilization of dichloromethane originally present at 1 mg/l to be 21 ± 3 minutes when stirred at 200 rpm in water at approximately 25°C in an open container. Removal of 90 percent of the dichloromethane under the same conditions required 60 minutes. For chloroaliphatics in general, stirring speed was found to have a marked effect on volatilization rate. With minimal stirring (15 seconds every five minutes), the time required for 50 percent depletion of dichloromethane was approximately 90 minutes, which is four times greater than observed with constant stirring. The presence of sodium chloride at a 3 percent concentration, as in seawater, effected a 10 percent decrease in the evaporative rate.

From the results of the above experiments, Dilling et al. (1975) conclude that evaporation is probably the major pathway by which dichloromethane is lost from water. In this context, Dilling et al. (1975) are careful to point out the difficulties encountered in extrapolating their laboratory results to real-world conditions, where the concentration of the organic solute would probably be very much less than 1 mg/l and where surface and bulk agitation would be highly variable. Although the data appear to be valid on a relative basis (i.e., correctly illustrating the relative rates of volatilization of chlorinated aliphatics), they cannot be used as absolute measures of volatilization rates from natural waters. For the purposes of this document, the data are used as rough-order-of-magnitude indications of the importance of volatilization relative to other transport and fate processes, with the strong effects of agitation considered. The validity of this application has not been established.

A subsequent study by Dilling (1977) was conducted using the same experimental conditions as in the aforementioned investigation, and an average half-life of 25.2 minutes with respect to evaporation of 0.99 mg/l dichloromethane was obtained. The purpose of this subsequent study was to use the experimental data that was obtained to test two theoretical models formulated to predict evaporative rates of slightly soluble organic compounds from water. Dilling (1977) found that the theoretical model proposed by Mackay and Wolkoff (1973) failed to predict evaporative half-lives, but that the theoretical model of Mackay and Leinonen (1975) using the parameters of Liss and Slater (1974) correlated well with the experimental half-lives obtained. For example, the evaporative half-life obtained experimentally by Dilling (1977) was 18 to 25 minutes as compared to a 20.7 minute evaporative half-life calculated by the Mackay and Leinonen (1975) model using the parameters of Liss and Slater (1974), whereas the half life predicted by the Mackay and Wolkoff (1973) model was 2.23 minutes.

Dilling (1977), however, comments that the apparent numerical agreement between his data and the values predicted by the Mackay and Leinonen (1975) model may be fortuitous. Estimates of volatilization rates based on the Mackay and Leinonen (1975) model depend primarily on liquid-gas phase exchange rate constants, whereas the experimental model of Dilling et al. (1975) and Dilling (1977) is controlled by the rate of stirring and the wind velocity across the surface of the water.

Pearson and McConnell (1975) suggest that the presence of dichloromethane and other halogenated aliphatics in ambient waters is due to absorption of chloroorganics from the atmosphere by water and return to the earth via precipitation. Aerial transport of these chloroorganics is indicated by Pearson and McConnell (1975) to play a major role in the wider distribution of these compounds and to account for their presence in upland waters.

39.4.5 Sorption

Dilling et al. (1975) carried out two closed system experiments where solute loss could occur only by adsorption. Dry bentonite clay at

375 mg/l was introduced into a sealed solution and in ten minutes there occurred approximately a ten percent adsorption of dichloromethane and other chloroaliphatics onto the clay. When the amount of clay added to the closed system was doubled (750 mg/l), 22 percent solute loss via adsorption was noted after 30 minutes. There was no further solute adsorption after this time. The authors indicated that there appeared to be little selectivity (with respect to the adsorption process) among the various chlorinated compounds used in the experiment. The authors observed some adsorption of dichloromethane by dry powdered dolomitic limestone, but, again, no selectivity among the solute compounds was observed.

In a sealed system with approximately 500 mg/l peat moss, approximately 40 percent of the dichloromethane was adsorbed onto the peat moss after 10 minutes. At longer times, no further solute removal was noted.

39.4.6 Bioaccumulation

According to Kopperman et al (1976), not all organochlorine compounds bioaccumulate to high levels. The data suggest that polar compounds are more easily biodegraded, whereas non-polar, highly lipophilic compounds accumulate. Neely et al. (1974) have shown that bioaccumulation is directly related to the octanol/water partition coefficient (P) of the compound. The log octanol/water partition coefficient (log P) of dichloromethane is 1.25 (Hansch et al. 1975), indicating that dichloromethane is not highly lipophilic and probably would not exhibit a significant tendency to bioaccumulate in organisms.

39.4.7 Biotransformation and Biodegradation

No information pertaining specifically to the biodegradation of dichloromethane was found. Thom and Agg (1975) have included dichloromethane in a list of synthetic organic chemicals which should be degradable by biological sewage treatment, provided suitable acclimatization can be achieved. They note, however, that not many compounds in this list occur in nature, and, as a result, it is unlikely that microorganisms already possess the ability to destroy them. Thom and Agg (1975) consider dichloromethane to be potentially biodegradable.

39.4.8 Other Reactions

Rook (1977) has suggested that dichloromethane, which has been found in finished drinking water, may be present in such chlorinated water due to the haloform reaction. Stated simply, the haloform reaction is an aqueous chlorination reaction which can occur during the treatment of water supplies, generally in alkaline solution, with organic compounds containing the acetyl group or with structures that may be oxidized readily to the acetyl group (Morris 1975). The three hydrogens of the methyl component of the acetyl group are successively replaced by chlorine or other halogen, and then the carbon bond to the carbonyl group is hydrolyzed giving rise to a haloform and a carboxylic acid (Morris 1975). The simplified reaction is given below:

$$CH_3COR + 3HOCl \longrightarrow CCl_3COR + 3H_2O \qquad (1)$$

$$CCl_3COR + H_2O \longrightarrow CHCl_3 + RCOOH \qquad (2)$$

It has been suggested that organic compounds that have a structure equivalent to an acetyl group are present in the form of humic materials (specifically, fulvic acids) which cause the yellow to brown stain of surface waters (Rook 1974; Rook 1977; Morris 1975). The carbon between two meta-positioned OH-groups of a hydroxylated aromatic ring is proposed as the most reactive site for haloform formation (Rook 1977).

39.5 Data Summary

Table 39-1 summarizes the aquatic fate data discussed above. The rate of oxidation that is presented is a photooxidation rate and refers to the rate of reaction of volatilized dichloromethane with hydroxyl radicals in the troposphere. Such photooxidation appears to be the major environmental fate of dichloromethane, and is a result of the high vapor pressure of this compound which causes it to volatilize rapidly from water into the atmosphere. Any dichloromethane that remains unreacted in the troposphere will diffuse upward and be photodissociated in the stratosphere. Alternatively, atmospheric dichloromethane may be returned to the earth in precipitation.

Table 39-1

Summary of Aquatic Fate of Dichloromethane

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Probably not significant in aquatic systems, but may occur in the stratosphere.	-	-	Medium
Oxidation[a]	The predominant fate of this compound appears to be attack by hydroxyl radicals in the troposphere; oxidation in water is not important.	$1.04 \times 10^{-13} cm^3 sec^{-1}$	0.30 years[b]	Medium
Hydrolysis	Probably not a significant fate.	$1.9 \times 10^{-8} sec^{-1}$[c]	417 days	Medium
Volatilization	Primary transport process from the aquatic environment.	-	27 minutes[d]	Medium
Sorption	Probably not significant.	-	-	Low
Bioaccumulation	Probably does not significantly bioaccumulate in organisms.	-	-	Low
Biotransformation/ Biodegradation	Probably occurs but at an extremely slow rate.	-	-	Low

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a. The predominant environmental process which is thought to determine the fate of the compound.

b. Reported as a lifetime of 0.30 years.

c. Hydrolysis rate is probably a minimum rate.

d. Half-lives are on the order of several minutes to a few hours, depending on the degree of agitation; the stated rate is based on the experimental results of Dilling (1977) and Dilling et al. (1975) using a stirred container.

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40. TRICHLOROMETHANE (CHLOROFORM)

40.1 Statement of Probable Fate

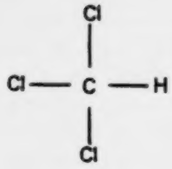
Volatilization is the major transport process for removal of trichloromethane (chloroform) from aquatic systems. Once in the troposphere, trichloromethane is attacked by hydroxyl radicals with the subsequent formation of phosgene ($COCl_2$) and possibly the ClO radical as principal, initial products. The portion unreacted in the troposphere may be returned to the earth in precipitation or on particulates, and a small amount may diffuse upward to the stratosphere, where it photodissociates via interaction with high-energy ultraviolet light.

Based on the information reviewed, it appears that neither oxidation nor hydrolysis is an important fate process for trichloromethane in the aquatic environment. No information was found to indicate that either bioaccumulation or sorption is an important process for trichloromethane in the aquatic environment.

40.2 Identification

Trichloromethane is known to be ubiquitous in the environment; its presence has been detected in finished drinking water (Environmental Protection Agency 1975a; Morita *et al.* 1974), in marine waters and sediments (Pearson and McConnell 1975; McConnell *et al.* 1975), in rainwater (Pearson and McConnell 1975), in wastewater effluents (Glaze and Henderson 1975), and in the atmosphere (Singh *et al.* 1978; Environmental Protection Agency 1975b, Lillian *et al.* 1975).

The chemical structure of trichloromethane is shown below.



$$\begin{array}{ccc} & Cl & \\ & | & \\ Cl - & C & - H \\ & | & \\ & Cl & \end{array}$$

Trichloromethane

CAS NO. 67-66-3
TSL NO. FS91000

Alternate Name

Chloroform

40.3 Physical Properties

The general physical properties of trichloromethane are given below.

Molecular weight (Weast 1977)	119.38
Melting point (Weast 1977)	-63.5°C
Boiling point at 760 torr (Weast 1977)	61.7°C
Vapor pressure at 20°C (Pearson and McConnell 1975)	150.5 torr
Solubility in water at 20°C (Pearson and McConnell 1975)	8,200 mg/l
Log octanol/water partition coefficient (Hansch et al. 1975)	1.97

40.4 Summary of Fate Data

40.4.1 Photolysis

Relatively little information pertaining specifically to the rate of photolysis of trichloromethane in the aqueous environment under ambient conditions was found. Dilling et al. (1975) studied the rate of decomposition of trichloromethane at a 1 mg/l concentration in water in aerated sealed tubes and found little difference between the rate of disappearance of trichloromethane in tubes exposed to sunlight and those kept in darkness. After one year, an average (sample size = 2) of 36 percent of the trichloromethane had disappeared from samples kept in darkness as opposed to an average loss of 43.5 percent for samples exposed to sunlight. Another study by Jensen and Rosenberg (1975) compared the rate of disappearance of trichloromethane in a closed flask series in daylight and a closed aquarium system in darkness and found no significant difference in the two systems. The experimental results support the findings that trichloromethane absorbs light only at wavelengths well below the 290 nm tropospheric cutoff (Lillian et al. 1975) and, as a result, would not be expected to undergo direct photolysis below the ozone layer.

Trichloromethane absorbs ultraviolet light maximally at 175 nm (Lillian et al. 1975). This wavelength almost coincides with the wavelength region from 180 to 240 nm which is the wavelength range in which photodissociation in the stratosphere occurs (Robbins 1976). As a result, any trichloromethane which reaches the stratosphere would be expected to photodissociate, although the rate is unknown.

40.4.2 Oxidation

Dilling et al. (1975) conducted aqueous reactivity experiments in which there was a large excess of dissolved oxygen compared to the total amount of trichloromethane. The air space above the solution in the closed system contained approximately 90 times as much oxygen as was present in the saturated solution. The observed disappearance, which occurred at a rate much lower than rates of volatilzation from water of trichloromethane as reported by the same authors, was attributed primarily to ionic hydrolysis rather than oxidation. On this basis it is concluded that oxidation in the aqueous phase is not an important process for trichloromethane.

Due to the high vapor pressure of trichloromethane, volatilization to the atmosphere is quite rapid. Once in the troposphere, trichloromethane is attacked by hydroxyl radicals via hydrogen abstraction (Hanst 1978; Spence et al. 1976; Environmental Protection Agency 1975b; Cox et al. 1976). The product of this reaction is reported to be a CCl_3 radical which reacts with oxygen to yield phosgene ($COCl_2$) and possibly chlorine oxide (ClO) radicals (Spence et al. 1976; Hanst 1978; Environmental Protection Agency 1975b). Neither of these initial products would be expected to persist; phosgene is readily hydrolyzed to HCl and CO_2 (Morrison and Boyd 1973).

Reaction with hydroxyl radicals is stated by Yung et al. (1975) to be the primary mechanism for the removal of trichloromethane from the atmosphere. The estimated atmospheric lifetime for trichloromethane is reported to be about two to three months (Environmental Protection Agency 1975b; Yung et al. 1975). According to Cox et al. (1976), trichloromethane reacts with hydroxyl radicals present in the troposphere at a rate of $16.8 \times 10^{-14} cm^3 sec^{-1}$, which corresponds to a reported tropospheric lifetime (time for reduction to 1/e of the original concentration) of 0.19 years. Yung et al. (1975) report a bimolecular rate constant of $1.0 \times 10^{-12} \exp(-630/T)\ cm^3 sec^{-1}$ ($11.9 \times 10^{14}\ cm^3 sec^{-1}$ at 23°C), corresponding to a tropospheric lifetime of approximately 10^7 sec (0.32 years).

At a tropospheric lifetime of 0.2 to 0.3 years, and assuming a troposphere-to-stratosphere turnover time (time for all but 1/e of tropospheric air to diffuse into the stratosphere) of 30 years, on the order of one percent of tropospheric trichloromethane would eventually reach the stratosphere.

40.4.3 Hydrolysis

A maximum hydrolytic half-life of 3,500 years has been estimated for trichloromethane at pH 7 and 25°C (Radding et al. 1977) by extrapolation from data at 100-150°C. This corresponds to a first-order rate constant for hydrolysis of trichloromethane of 6.9 x 10^{-12}sec^{-1} (1.8 x 10^{-4} month $^{-1}$) (Radding et al. 1977). The validity of the extrapolation method has not been established, and the estimated hydrolytic half-life of 3,500 years is in sharp contrast to the half-life of approximately 15 months, corresponding to a first-order rate of 0.045 month^{-1}, attributed primarily to ionic hydrolysis by Dilling et al. (1975) from the aqueous reactivity experiments described previously. Since oxidation and vapor-phase hydrolysis could each have occurred in the system used, the rate reported must be regarded as an upper limit for aqueous-phase hydrolysis of trichloromethane. It should be noted that a similar discrepancy in values exists for dichloromethane (a compound structurally similar to chloroform) with respect to the half-life of hydrolysis estimated by Radding et al. (1977) by extrapolation from data at 100-150°C and the experimental value obtained by Dilling et al. (1975) at 25°C.

40.4.4 Volatilization

Dilling et al. (1975) estimated the experimental half-life for volatilization of trichloromethane originally present at 1 mg/l to be 21 ± 4 minutes when stirred at 200 rpm in water at approximately 25°C in an open container. Removal of 90 percent of the trichloromethane under the same conditions required 62 minutes. For chloroaliphatics in general, stirring speed was found to have a marked effect on volatilization rate. With no stirring except 15 seconds every five minutes, the time required for 50 percent depletion of trichloromethane was greater than 90 minutes, which is on the order of four times greater than the stirred case for this compound. The presence of sodium chloride at a three percent concentration, as in seawater, caused about a ten percent decrease in the evaporation rate.

From the results of the above experiments, Dilling et al. (1975) conclude that evaporation is the major pathway by which trichloromethane, as well as the other chlorinated compounds, is lost from water. Dilling et al. (1975) are careful to point out the difficulties encountered in extrapolating their laboratory results to real-world conditions, where the concentration of the organic solute would probably be very much less than 1 mg/l and where surface and bulk agitation would be highly variable. Although the data appear to be valid on a relative basis (i.e., correctly illustrating the relative rates of volatilization of chlorinated aliphatics), they cannot be used as absolute measures of volatilization rates from natural waters. For the purposes of this document, the data are used as rough-order of magnitude indications of the importance of volatilization relative to other transport and fate processes, with the strong effects of agitation considered. The validity of this application has not been established.

A subsequent study by Dilling (1977) was conducted using the same experimental conditions as in the 1975 study, and an average evaporative half-life of 25.7 minutes for 0.96 mg/l trichloromethane was obtained. The purpose of this subsequent study was to use the experimental data obtained to test two theoretical models formulated to predict evaporative rates of slightly soluble organic compounds from water. Dilling (1977) found that the theoretical model of Mackay and Wolkoff (1973) failed to predict evaporative half-lives, but that the calculated evaporative half-lives from the theoretical model of Mackay and Leinonen (1975) using parameters from Liss and Slater (1974), correlated well with the experimental evaporative half-lives obtained by Dilling (1977). For example, the evaporative half-life obtained experimentally by Dilling (1977) was 19 to 26 minutes as compared to 23.7 minutes predicted by the Mackay and Leinonen (1975) model and 1.46 minutes predicted by the Mackay and Wolkoff (1973) model.

Dilling (1977), however, comments that the apparent numerical agreement between his data and the values predicted by the Mackay and Leinonen (1975) model may be fortuitous. Estimates of volatilization rates based on the Mackay and Leinonen (1975) model depend primarily on liquid-gas phase exchange rate constants, whereas the experimental model of Dilling et al. (1975) and Dilling (1977) is controlled by the rate of stirring and the wind velocity across the surface of the water.

Pearson and McConnell (1975) suggest that the presence of trichloromethane and other halogenated aliphatics in ambient waters is due to absorption of chloroorganics from the atmosphere by water droplets and return to the earth during precipitation. Aerial transport of these chloroorganics is indicated by Pearson and McConnell (1975) to play a major role in the wider distribution of these compounds and accounts for their presence in upland waters.

A study by Jensen and Rosenberg (1975) indicates that volatilization of trichloromethane from water proceeds more rapidily than photolysis, oxidation, or hydrolysis in the aqueous medium. An initial concentration of between 0.1 to 1 mg/l trichloromethane in 20 liters of water was found to decrease 50 to 60 percent after eight days in an aquarium kept in light and partly open. Trichloromethane initially present at the same concentration in a closed system exposed to daylight and a closed system exposed to dark exhibited less than five percent loss in 8 days. Assuming that all processes involved were first-order, then the rate of volatilization appears to be an order of magnitude larger than the summation of the rates for degradative and other loss processes in the closed system where volatilization could not occur.

40.4.5 Sorption

Dilling et al. (1975) carried out two closed system experiments where the solute loss could be only by adsorption. Dry bentonite clay at 375 mg/l was introduced into a sealed solution, and after ten minutes there was approximately a ten percent adsorption of trichloromethane and other chlorinated compounds by the clay. When the amount of clay added to the closed system was doubled (750 mg/l) there was 22 percent solute loss via adsorption after 30 minutes. There was no further solute adsorption after this time. The authors indicated that there appeared to be little selectivity of the clay among the various chlorinated compounds used. Some adsorption of trichloromethane and other short-chain chloroaliphatics by dry powdered dolomitic limestone was observed, but again without selectivity for specific solutes.

Dilling et al. (1975) also found that, in a sealed system with approximately 500 mg/l peat moss, approximately 40 percent of the trichloromethane solute adsorbed in 10 minutes. At longer times, no further solute removal was noted.

Pearson and McConnell (1975) found that the concentrations of chloroorganics in Liverpool Bay (England) sediments varied from a few parts per trillion (by mass) to a maximum of 4000 parts per trillion trichloromethane. Samples of marine sediment from Liverpool Bay contained the same compounds as the overlying waters. There was, however, no significant correlation found between the concentration of trichloromethane in marine sediment and the concentration in the water above the sediment at the time the samples were taken (Pearson and McConnell 1975; McConnell et al. 1975). In addition, there was no correlation between high concentrations of trichloromethane and geographical features, as was noticed for several other compounds, nor was there any correlation between the trichloromethane concentration in the sediment and particle size. McConnell et al. (1975), however, did note that coarse gravels had little adsorptive capacity for trichloromethane, whereas sediments rich in organic detritus had a much higher adsorptive capacity. In summary, there was no clear evidence of selective concentration of trichloromethane in sediments.

40.4.6 Bioaccumulation

According to Kopperman et al. (1976), not all organochlorine compounds bioaccumulate to high levels. The data suggest that polar compounds are more easily biodegraded, whereas non-polar, highly lipophilic compounds accumulate. Neely et al. (1974) have shown that bioaccumulation is directly related to the octanol/water partition coefficient (P) of the compound. The log octanol/water partition coefficient (log P) of trichloromethane is 1.97 (Hansch et al. 1975; Chiou et al. 1977; Leo et al. 1971), thus indicating a possible tendency of this compound to bioaccumulate under conditions of constant exposure.

Evidence for weak to moderate bioaccumulation of trichloromethane by marine organisms is reported by Pearson and McConnell (1975). These authors, however, have indicated that although trichloromethane is somewhat lipophilic and tends to be found in higher concentrations in fatty tissues, there is no evidence for biomagnification of trichloromethane in aquatic food chains.

40.4.7 Biotransformation and Biodegradation

According to Pearson and McConnell (1975), only completely sealed systems such as the standard BOD (biochemical oxygen demand) bottle technique can be used to measure biochemical degradation of volatile compounds such as trichloromethane. The BOD bottle experiments of Pearson and McConnell (1975) have been unable to demonstrate any significant oxygen absorption from compounds containing only C, H, and Cl, thus indicating that biochemical degradation of such compounds is indeed very slow.

Thom and Agg (1975) have included trichloromethane in a list of synthetic organic chemicals which should be degradable by biological sewage treatment, provided suitable acclimatization can be achieved.

40.4.8 Other Reactions

Rook (1977) has suggested that trichloromethane, which has been found in finished drinking water, may be present in such chlorinated water due to the haloform reaction. Stated simply, the haloform reaction is an aqueous chlorination reaction, connected with the treatment of water supplies, which occurs generally in alkaline solution (pH $\geq$ 5) with organic compounds containing the acetyl group or with structures that may be readily oxidized to the acetyl group (Morris 1975). The three hydrogens on the methyl component of the acetyl group are successively replaced by chlorine or other halogen, and then the carbon bond to the carbonyl group is split giving rise to a haloform and a carboxylic acid (Morris 1975). The simplified reaction is given below:

$$CH_3COR + 3HOCl \longrightarrow CCl_3COR + 3H_2O \qquad (1)$$
$$CCl_3COR + H_2O \longrightarrow CHCl_3 + RCOOH \qquad (2)$$

It has been suggested that organic compounds that have a structure equivalent to an acetyl group are present in the form of humic materials (such as fulvic acids) which cause the yellow to brown stain of surface waters (Rook 1974; Rook 1977; Morris 1975). Specifically, the carbon between two meta-positioned OH-groups of a hydroxylated aromatic ring is proposed as the most reactive site for haloform formation (Rook 1977).

40.5 Data Summary

Table 40-1 summarizes the aquatic fate of trichloromethane. Oxidation rates given are photooxidation rates and refer to the rate of reaction of trichloromethane with hydroxyl radicals in the troposphere.

The primary fate of trichloromethane is believed to be photooxidation in the troposphere, a direct result of the high vapor pressure of this compound which causes it to volatilize rapidly from water into the atmosphere. Once in the troposphere, trichloromethane is attacked by hydroxyl radicals resulting in the subsequent formation of phosgene and chlorine oxide as principal products. Any unreacted portion of trichloromethane in the troposphere diffuses upward and undergoes photodissociation above the ozone layer, or is absorbed by water and returned to the earth via precipitation.

Table 40-1

Summary of Aquatic Fate of Trichloromethane

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Probably not significant in aquatic systems.	-	-	Medium
Oxidation[a]	The primary fate of this compound is attack by hydroxyl radicals in the troposphere.	$16.8 \times 10^{-14} cm^3 sec^{-1}$ $11.9 \times 10^{-14} cm^3 sec^{-1}$	0.19 years[b] 0.32 years[b]	High
Hydrolysis	Is probably not a significant fate process.	$6.9 \times 10^{-12} sec^{-1}$ 0.045 months^{-1}	3,500 years[c] 15 months[d]	Medium
Volatilization	The primary transport process from the aquatic environment.	-	21 ± 4 minutes[e]	Medium
Sorption	Probably not significant.			Medium
Bioaccumulation	Weak to moderate bioaccumulation; no evidence of biomagnification of trichloromethane in marine food chain.			Medium
Biotransformation/ Biodegradation	No specific information; in the sea, many invertebrates metabolize halogens.			Low

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a. The predominant environmental process which is thought to determine the fate of this compound.

b. Reported as a lifetime (time for reduction to 1/e of original concentration) of 0.19 years and 0.32 years, respectively.

c. Hydrolysis rate is a minimum rate.

d. Hydrolysis rate is a maximum rate.

e. Half-lives are on the order of several minutes to a few hours and depend on the degree of agitation; this rate is based on the experimental results of Dilling (1977) and Dilling *et al*. (1975) using a stirred system.

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41. TETRACHLOROMETHANE (CARBON TETRACHLORIDE)

41.1 Statement of Probable Fate

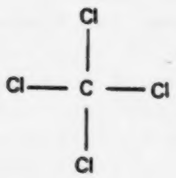
Volatilization is the major transport process for removal of tetrachloromethane from aquatic systems. Once in the troposphere, tetrachloromethane remains stable; it exhibits an extremely slow rate of reaction with hydroxyl radicals present in the troposphere. Tetrachloromethane eventually diffuses into the stratosphere or is carried back to the earth during the precipitation process. Once in the stratosphere tetrachloromethane is degraded on exposure to shorter wavelength, higher energy ultraviolet light to eventually form phosgene as the principal initial product.

Based on the information reviewed, it does not appear that oxidation is an important fate process of tetrachloromethane in the aquatic environment. Evidence for sorption, bioaccumulation and biotransformation, hydrolysis, and biodegradation is inconclusive.

41.2 Identification

Tetrachloromethane is known to be ubiquitous in the environment; its presence has been detected in finished drinking water (Environmental Protection Agency 1975a), in fresh water and rainwater (Pearson and McConnell 1975), in marine water and sediment (Pearson and McConnell 1975; McConnell _et al_. 1975), and in the atmosphere (Singh _et al_. 1978; Environmental Protection Agency 1975b; Lillian _et al_. 1975; Lovelock _et al_. 1973).

The chemical structure of tetrachloromethane is shown below.



Tetrachloromethane

CAS NO. 56-23-5
TSL NO. FG 49000

Alternate Names

Carbon tetrachloride
Methane tetrachloride
Perchloromethane
Benzinoform

41.3 Physical Properties

The general physical properties of tetrachloromethane are given below.

Molecular weight (Weast 1977)	153.82
Melting point (Weast 1977)	-22.9°C
Boiling point at 760 torr (Weast 1977)	76.54°C
Vapor pressure at 20°C (Pearson and McConnell 1975)	90 torr
Solubility in water at 20°C (Pearson and McConnell 1975)	785 mg/l
Log octanol/water partition coefficient (Neely *et al.* 1974)	2.64

41.4 Summary of Fate Data

41.4.1 Photolysis

No information was found pertaining to the rate of photolysis of tetrachloromethane in the aqueous environment under ambient conditions.

Due to the high vapor pressure of tetrachloromethane, volatilization to the atmosphere is quite rapid. Tetrachloromethane is, however, tropospherically stable (Singh *et al.* 1978; Environmental Protection Agency 1975b; Hanst 1978; Lillian *et al.* 1975; Cox *et al.* 1976) and does not react significantly with hydroxyl radicals present in the troposphere. In addition, tetrachloromethane does not photodissociate in the troposphere since this compound has no chromophores which absorb in the visible or near ultraviolet region of the electromagnetic spectrum (Jaffé and Orchin 1962).

The tropospherically stable tetrachloromethane eventually diffuses into the stratosphere (Hanst 1978; National Research Council 1978), although some tetrachloromethane is theorized to be washed out of the atmosphere and back to the lithosphere and hydrosphere during the precipitation process (Pearson and McConnell 1975). That portion of the tetrachloromethane which diffuses to the stratosphere is degraded on exposure to higher energy, shorter wavelength ultraviolet light to form

CCl_3 radicals and chlorine atoms. The CCl_3 radicals are oxidized to form phosgene which also undergoes photodissociation in the stratosphere with the subsequent release of more chlorine atoms (Hanst 1978; National Research Council 1978). Chlorine atoms, released by reactions such as these, are theorized to be catalysts in the destruction of the ozone layer of the earth (Hanst 1978; National Research Council 1978).

41.4.2 Oxidation

No information was found pertaining to the oxidation of tetrachloromethane in the aquatic environment under ambient conditions. In addition, tetrachloromethane is known to be tropospherically stable (Singh et al. 1975; Environmental Protection Agency 1975b; Hanst 1978; Lillian et al. 1975; Cox et al. 1976) and, therefore, does not react significantly with hydroxyl radicals present in the troposphere. For instance, the bimolecular rate of reaction for tetrachloromethane with hydroxyl radicals is reported to be less than $1 \times 10^{-16} cm^3 sec^{-1}$ with a corresponding reported tropospheric lifetime (time for reduction to 1/e of initial concentration) of greater than 330 years (Cox et al. 1976). As a result, photooxidation of tetrachloromethane would not be expected to play a significant role in the fate of this compound.

Using the minimum tropospheric lifetime of 330 years, and assuming a troposphere-to-stratosphere turnover time (time for all but 1/e of tropospheric air to diffuse into the stratosphere) of 30 years, the fraction of tropospheric tetrachloromethane eventually reaching the stratosphere would be over 90 pecent.

41.4.3 Hydrolysis

A maximum hydrolytic half-life of 7,000 years has been calculated tetachloromethane at a 1 mg/l concentration at pH 7 and 25°C; at a 1000 mg/l concentration under the same conditions a hydrolytic half-life of 7 years has been calculated for tetrachloromethane (Mabey and Mill 1978; Radding et al. 1977). These half-life values correspond to a reported second-order rate of hydrolysis for tetrachloromethane of 4.8×10^{-7} $mol^{-1}sec^{-1}$, and are based on extrapolation of data at 100°-150°C.

Lovelock et al. (1973) have suggested that tetrachloromethane may undergo hydrolysis in the ocean as evidenced from the fall-off in tetrachloromethane concentration with depth in ocean water samples. Thus, in addition to the stratosphere as a major sink for tetrachloromethane, the oceans may prove to be a significant sink as well.

41.4.4 Volatilization

Volatilization is the most important transport process for the removal of tetrachloromethane from aquatic systems. Dilling et al. (1975) estimated the experimental half-life for volatilization of tetrachloromethane originally praesent at 1 mg/l to be 29 minutes when stirred at 100 rpm in water at approximately 25°C in an open container. Removal of 90 percent of the tetrachloromethane under the same conditions required 97 minutes. For chloroaliphatics in general, stirring speed was found to have a marked effect on volatilization rate. Stirring intermittently for 15 seconds every five minutes, the time required for 50 percent depletion of trichloromethane and dichloromethane, analogues of tetrachloromethane, was greater than 90 minutes, or four times greater than was observed during constant stirring. Dilling et al. (1975) are careful to point out the diffculties encountered in extrapolating their laboratory results to real-world conditions, where the concentration of the organic solute would probably be very much less than 1 mg/l and where surface and bulk agitation would be highly variable. Although the data appear to be valid on a relative basis (i.e., correctly illustrating the relative rates of volatilization of chlorinated aliphatics), they cannot be used as absolute measures of volatilization rates from natural waters. For the purposes of this document, the data are used as rough-order-of-magnitude indications of the importance of volatilization relative to other transport and fate processes, with the strong effects of agitation considered. The validity of this application has not been established.

A subsequent study by Dilling (1977) was conducted using the same experimental conditions as the 1975 study, and an evaporative half-life for 0.90 mg/l tetrachloromethane of 28.8 minutes (average of four) was obtained. The purpose of this subsequent study was to use the experimental data previously obtained to test two theoretical models which may be used to predict evaporation rates of slightly soluble organic compounds from water. Dilling (1977) found that the theoretical model by Mackay and Wolkoff (1973) failed to predict evaporation half-lives, but that the model of Mackay and Leinonen (1975) using parameters from Liss and Slater (1974) correlated well with the experimental half-lives obtained by Dilling (1977). For example, the evaporative half-life obtained experimentally by Dilling (1977) was 29 minutes, compared to 25.5 minutes predicted by the Mackay and Leinonen (1975) model and 0.20 minutes predicted by the Mackay and Wolkoff (1973) model.

Dilling (1977), however, comments that the apparent numerical agreement between his data and the values predicted by the Mackay and Leinonen (1975) model may be fortuitous. Estimates of volatilization rates based on the Mackay and Leinonen (1975) model depend primarily on liquid-gas phase exchange rate constants, whereas the experimental model of Dilling et al. (1975) and Dilling (1977) is controlled by the rate of stirring and the wind velocity across the surface of the water.

Pearson and McConnell (1975) suggest that the presence of tetrachloromethane, as well as other halogenated aliphatics, in ambient waters is due to the absorption of chloroorganics from the atmosphere by water. This process is thought to occur most effectively when the atmosphere is scrubbed as in the precipitation process. Aerial transport of these chloroorganics is indicated by Pearson and McConnell (1975) to play a major role in the wider distribution of these compounds and accounts for their presence in upland waters.

41.4.5 Sorption

There is little information pertaining specifically to adsorption of tetrachloromethane onto sediments. Pearson and McConnell (1975) found that the concentrations of chloroorganics in Liverpool Bay sediments in England varied from a few ng/l to a maximum of 5500 ng/l 1,1,1-trichloroethane plus tetrachloromethane combined. Samples of marine sediment from Liverpool Bay contained the same compounds as the overlying waters. Due to the inability of the sampling technique to resolve tetrachloromethane and 1,1,1-trichloroethane, it could not be determined whether a correlation existed between the concentrations of tetrachloromethane in marine sediments and interstitial waters above the sediments at the time the samples were taken (Pearson and McConnell 1975; McConnell et al. 1975). In addition, it is unknown whether a correlation existed between high concentrations and geographical features, as was noticed in the case of the water samples for several compounds, or whether there was a relationship between the concentration in the sediment and particle size. McConnell et al. (1975) did note, however, that coarse gravels had little adsorptive capacity for tetrachloromethane, whereas sediments rich in organic detritus had a much higher adsorptive capacity. In summary, there was no clear evidence of selective concentration of tetrachloromethane in sediments.

41.4.6 Bioaccumulation

According to Kopperman et al. (1976), not all organochlorine compounds bioaccumulate to high levels. The data suggest that polar compounds are more easily biodegraded, whereas non-polar, highly lipophilic compounds accumulate. Neely et al. (1974) have shown that bioaccumulation is directly related to the octanol/water partition coefficient (P) of the compound. The log octanol/water partition coefficient (log P) of tetrachloromethane is 2.64 (Neely et al. 1974; Chiou et al. 1977; Leo et al. 1971), indicating a tendency for this compound to bioaccumulate under conditions of constant exposure. Pearson and McConnell (1975), however, indicate that although tetrachloromethane, and other organochlorines examined, are somewhat lipophilic and tend to be found at higher concentrations in fatty tissues, there is no evidence for the biomagnification of tetrachloromethane or other short-chain choroaliphatics in food chains. The difficulties encountered with the analytical methods in the Pearson and McConnell (1975) study make estimates of bioaccumulation based on their experimental results somewhat unreliable.

41.4.7 Biotransformation and Biodegradation

No information was found pertaining specifically to the biodegradation of tetrachloromethane. In the sea, however, it is known that many species of brown seaweed, molluscs, sponges, and bacteria metabolize halogens (Anonymous 1977).

According to Pearson and McConnell (1975) only completely sealed systems, such as the standard BOD (biochemical oxygen demand) bottle technique, can be used to measure biochemical degradation of volatile compounds such as tetrachloromethane. The BOD bottle experiments of Pearson and McConnell do not demonstrate any significant oxygen absorption from compounds containing only C, H, and Cl, thus indicating that biochemical degradation of such compounds is indeed very slow.

Thom and Agg (1975) have included tetrachloromethane in a list of synthetic organic chemicals which should be degradable by biological sewage treatment methods provided suitable acclimatization can be achieved. They note, however, that not many compounds on the list occur free in nature, and, as a result, it is unlikely that microorganisms already possess the ability to destroy them.

41.5 Data Summary

Table 41-1 summarizes the aquatic fate information discussed above. The oxidation rate is a photooxidation rate and refers to the rate at which tetrachloromethane is attacked by hydroxyl radicals in the troposphere.

The ultimate fate of tetrachloromethane is photodissociation in the stratosphere, an end result of the high vapor pressure of this compound which causes it to volatilize rapidly into the atmosphere. Once in the troposphere, tetrachloromethane remains relatively stable and eventually diffuses into the stratosphere or is carried back to the earth during the precipitation process. Once in the stratosphere, tetrachloromethane is degraded on exposure to shorter wavelength, higher energy ultraviolet light.

Table 41-1

Summary of Aquatic Fate of Tetrachloromethane

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis[a]	Probably not significant in aquatic systems. Photolysis in the stratosphere is the primary fate of this compound.	-	-	High
Oxidation	Not a significant fate process for this compound.	$<1 \times 10^{-16} cm^3 sec^{-1}$	330 years[b]	High
Hydrolysis	Is too slow to be a significant fate process.	$4.8 \times 10^{-7} M^{-1} sec^{-1}$	7000 years[c]	Medium
Volatilization	The primary transport process from the aquatic environment.	-	~29 minutes[d]	Medium
Sorption	No clear evidence of selective concentration of carbon tetrachloride in sediments.	-	-	Low
Bioaccumulation	Evidence is inconclusive.	-	-	-
Biotransformation/ Biodegradation	Probably occurs at an extremely slow rate.	-	-	Low

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a. The predominant environmental process which is thought to determine the fate of the compound.

b. Reported as a lifetime (time for reduction to 1/e of initial concentration).

c. Hydrolysis rate is a minimum rate.

d. Half-lives are on the order of 29 minutes to a few hours, depending on the degree of agitation in the system; the value stated was determined under conditions of continuous mechanical stirring at 200 rpm.

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42. CHLOROETHANE (ETHYL CHLORIDE)

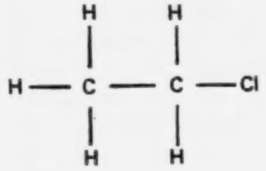
42.1 Statement of Probable Fate

Information found pertaining specifically to chloroethane is relatively scant. Much of the information presented herein has been extrapolated from more thoroughly studied analogues of chloroethane. Based on the material presented, one can predict with low to medium confidence that the important fate processes for chloroethane are photooxidation in the atmosphere and hydrolysis. The predominant fate process cannot as yet be identified with certainty.

42.2 Identification

Chloroethane has been detected in finished drinking water by the National Organics Reconnaissance Survey (Environmental Protection Agency 1975a). Chloroethane is probably present in the atmosphere but has not been detected either because of the small amounts emitted or because of rapid photooxidation in the troposphere (Environmental Protection Agency 1975b).

The chemical structure of chloroethane is shown below.



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & Cl \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

Chloroethane

CAS NO. 75-00-3
TSL NO. KH 75250

Alternate Names

Ethyl chloride
Monochloroethane
Hydrochloric ether
Muriatic ether

42.3 Physical Properties

The general physical properties of chloroethane are as follows.

Molecular weight (Weast 1977)	64.52
Melting point (Weast 1977)	-136.4°C
Boiling point at 760 torr (Weast 1977)	12.27°C

Vapor pressure at 20°C (Verschueren 1977)	1000 torr
Solubility in water at 20°C (Verschueren 1977)	5740 mg/l
Log octanol/water partition coefficient (Leo et al. 1971)	1.54

42.4 Summary of Fate Data

42.4.1 Photolysis

No information pertaining specifically to the rate of photodissociation of chloroethane in the aqueous environment was found. Dilling et al. (1975) reported that, within experimental error, sunlight did not accelerate decomposition of such compounds as dichloromethane, trichloromethane, and 1,1,1-trichloroethane, all more highly chlorinated analogues of chloroethane, intially present at 1 mg/l concentrations in aerated water.

Photodissociation in the terrestrial environment would not be expected to occur for chloroethane since this compound has no chromophores which absorb in the visible or near ultraviolet region of the electromagnetic spectrum (Jaffé and Orchin 1962). The rate of reaction of chloroethane with hydroxyl radicals in the troposphere is relatively rapid, but if any unreacted material were to reach the stratosphere, it would be expected to undergo significant photodissociation due to the presence of higher energy, shorter wavelength ultraviolet light (Environmental Protection Agency 1975b). Formyl chloride, which is readily photolyzed, is reported as the principal initial photodissociation product of chloroethane (Environmental Protection Agency 1975b).

42.4.2 Oxidation

No information pertaining specifically to the oxidation of chloroethane in the aqueous environment was found. There is, however, some indirect evidence of a probable low potential for oxidation in aquatic systems. For instance, Dilling et al. (1975) conducted aqueous reactivity experiments in which there was a large excess of dissolved oxygen compared to the total amount of dichloromethane, trichloromethane, and 1,1,1-trichloroethane, compounds similar to dichloroethane. The loss of material noted, which was attributed to ionic hydrolysis rather than oxidation, was much slower than loss by volatilization of the compounds from water reported by the same authors. It is concluded that oxidation in aqueous systems is not an important process for chloroethane.

Due to the relatively high vapor pressure of chloroethane, volatilization to the atmosphere is expected to be quite rapid. Once in the troposphere, chloroethane is photooxidized relatively rapidly. Howard and Evenson (1976) report a bimolecular rate constant for reaction of chloroethane with hydroxyl radicals of 3.9 (± 0.7) x 10^{-13} cm^3 $molecule^{-1}$ sec^{-1} at 23°C. Assuming the tropospheric hydroxyl radical concentration to be 10^6 cm^{-3}, this rate corresponds to a lifetime (time to reach 1/e of the original concentration) on the order of one month. Other available data (Environmental Protection Agency 1975b) indicate an atmospheric half-life for chloroethane of three or four months, and indicate formyl chloride to be the principal initial photooxidation product. Formyl chloride is readily hydrolyzed (Morrison and Boyd 1973).

The fraction of tropospheric chloroethane eventually reaching the stratosphere via diffusion is probably less than one percent, based on a tropospheric lifetime on the order of one month and a troposphere-to-stratosphere turnover time (time for all but 1/e of tropospheric air to diffuse into the stratosphere) of 30 years. It should be noted that this estimation neglects the effects of chloroethane removal from the troposphere by other processes such as rainfall.

42.4.3 Hydrolysis

A maximum hydrolytic half-life of 40 days has been estimated for chloroethane at pH 7 and 25°C by extrapolation from data at 100-150°C, corresponding to a first-order rate constant for hydrolysis of chloroethane of 2.0 x 10^{-7} sec^{-1} (Radding *et al*. 1977). The validity of the extrapolation technique used has *not* been established. The apparently short hydrolytic half-life and high solubility in water of chloroethane indicate that hydrolysis may be an important fate process for this compound.

42.4.4 Volatilization

Dilling *et al*. (1975) estimated the experimental half-life for volatilization of chloroethane originally present at 1 mg/l to be 21 minutes when stirred at 200 rpm in water at approximately 25°C in an open container. Removal of 90 percent of the chloroethane under the same conditions required 79 minutes. For chloroaliphatics in general, stirring speed was found to have a marked effect on volatilization rate. When intermittent stirring of 15 seconds duration was provided every five minutes, the time required for 50 percent depletion of dichloromethane, trichloromethane, and 1,1,1-trichloroethane, analogues of chloroethane, was greater than 90 minutes. This is on the order of four times longer than with constant stirring.

Dilling et al. (1975) are careful to point out the difficulties encountered in extrapolating their laboratory results to real-world conditions, where the concentration of the organic solute would probably be very much less than 1 mg/l and where surface and bulk agitation would be highly variable. Although the data appear to be valid on a relative basis (i.e., correctly illustrating the relative rates of volatilization of chlorinated aliphatics), they cannot be used as absolute measures of volatilization rates from natural waters. For the purposes of this document, the data are used as rough-order-of-magnitude indications of the importance of volatilization relative to other transport and fate processes, with the strong effecs of agitation considered. The validity of this application has not been established.

A subsequent study by Dilling (1977) was conducted using the same experimental conditions as in the 1975 study, and an average evaporative half-life of 23.1 minutes was obtained for 1 mg/l chloroethane in water. The purpose of this subsequent study was to use the experimental data previously obtained to test two theoretical models which may be used to predict rates of evaporation of slightly soluble organic compounds from water. Dilling (1977) found that the theoretical model by Mackay and Wolkoff (1973) failed to predict evaporative half-lives , and that the theoretical model of Mackay and Leinonen (1975) using parameters of Liss and Slater (1974) correlated well with the experimental evaporative half-lives obtained. For example, the evaporative half-life obtained experimentally by Dilling (1977) was approximately 23 minutes compared to a 16.7 minute evaporative half-life predicted by the Mackay and Leinonen (1975) model and 0.50 minutes predicted by Mackay and Wolkoff (1973).

Dilling (1977), however, comments that the apparent numerical agreement between his data and the values predicted by the Mackay and Leinonen (1975) model may be fortuitous. Estimates of volatilization rates based on the Mackay and Leinonen (1975) model depend primarily on liquid-gas phase exchange rate constants, whereas the experimental model of Dilling et al. (1975) and Dilling (1977) is controlled by the rate of stirring and the wind velocity across the surface of the water.

Pearson and McConnell (1975) suggest that the presence of analogues of chloroethane (such as chloromethane, dichloromethane, trichloromethane, and 1,2-dichloroethane) in ambient waters is due to the absorption of these compounds from the atmosphere by water. This process is thought to occur most effectively when the atmosphere is scrubbed as in the precipitation process. Aerial transport of these halogenated aliphatics is indicated by Pearson and McConnell (1975) to play a major role in the wider distribution of these compounds and accounts for their presence in upland waters.

42.4.5 Sorption

No information pertaining specifically to the adsorption of chloroethane onto sediments was found. Dilling et al. (1975) carried out two closed system experiments on dichloromethane, trichloromethane, and 1,1,1-trichloroethane, analogues of chloroethane, where solute loss could be only by adsorption. Dry bentonite clay at 375 mg/l was introduced into a sealed solution and after ten minutes approximately ten percent of the chloroalkanes had been removed from solution, presumably through adsorption by the clay. When the amount of clay added to the closed system was doubled (750 mg/l) there was 22 percent solute loss after 30 minutes and no further solute adsorption after this time. The authors indicate that there appeared to be little selectivity among the various chlorinated compounds in the adsorption process. The authors observed some adsorption of dichloromethane, trichloromethane, and 1,1,1-trichloroethane (analogues of chloroethane) by dry powdered dolomitic limestone, but, again, no selectivity among the solutes was noted.

In sealed aqueous samples with approximately 500 mg/l peat moss, approximately 40 percent of dichloromethane, trichloromethane, and 1,1,1,-trichloroethane (analogues of chloroethane), was removed in 10 minutes. At longer times than 10 minutes, no further solute removal was noted. The subsequent decrease in the rate of disappearance of dichloromethane, trichloromethane, and 1,1,1,-trichloroethane, analogues of chloroethane, at longer time periods than 10 minutes was suggested to be due to gradual release or desorption of these analogues of chloroethane from the peat moss to the solution.

Pearson and McConnell (1975) found no clear evidence of selective concentrations by sediments of the chloroethane analogues trichloromethane, tetrachloromethane, and 1,1,1-trichloroethane.

42.4.6 Bioaccumulation

According to Kopperman et al. (1976) not all organochlorine compounds bioaccumulate to high levels. The data suggest that polar compounds are more easily biodegraded, and the non-polar (highly lipophilic) compounds accumulate. Neely et al. (1974) have shown that bioaccumulation is related to the octanol/water partition coefficient (P) of the compound. The log octanol/water partition coefficient (log P) of 1.54 (Leo et al. 1971) indicates that chloroethane will probably not bioaccumulate to any significant extent (see Methods section on bioaccumulation).

42.4.7 Biotransformation and Biodegradation

No information pertaining specifically to the rate of biodegradation of chloroethane in aquatic systems was found. According to Pearson and McConnell (1975) only completely sealed systems, such as the standard

BOD (biochemical oxygen demand) bottle technique, can be used to measure biochemical degradation of volatile compounds such as chloroethane. The BOD bottle experiments of Pearson and McConnell have been unable to demonstrate any significant oxygen absorption from compounds containing only C, H, and Cl, thus indicating that biochemical degradation of such compounds is indeed very slow. Literature references to microbial biodegradation are few and conflicting; the majority indicate that low molecular weight chloroaliphatics are not metabolized (Pearson and McConnell 1975; McConnell *et al*. 1975).

42.5 Data Summary

Table 42-1 summarizes the aquatic fate discussed above. The oxidation rate presented is an atmospheric photooxidation rate and refers to the rate of reaction of chloroethane with hydroxyl radicals in the troposphere.

The information found pertaining specifically to chloroethane is relatively scant. Based on the information presented above, it is concluded (with low to medium confidence) that the important fate processes for chloroethane are photooxidation in the atmosphere and hydrolysis, or both of these occurring concomitantly.

Table 42-1

Summary of Aquatic Fate of Chloroethane

Environmental Process[a]	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Based on extrapolation from more thoroughly studied analogues, it appears that photolysis in the aquatic environment is not significant.	-	-	Medium
Oxidation	Photooxidation in the troposphere appears to be one of the predominant fates of this compound; photooxidation in the aquatic environment probably occurs at a slow rate; direct oxidation at ambient conditions does not occur significantly in the aquatic or atmospheric environment.	3.9×10^{-13} $cm^3 molecule^{-1} sec^{-1}$	1-4 months[b]	Medium
Hydrolysis	May be a significant fate process.	$2.0\times10^{-7} sec^{-1}$	40 days[c]	Low to Medium
Volatilization	Probably the primary transport process.	-	~20 to 25 min.[d]	Medium
Sorption	Probably not important.	-	-	Low
Bioaccumulation	Probably does not significantly bioaccumulate.	-	-	Medium
Biotransformation/ Biodegradation	Probably occurs at a slow rate.	-	-	Low

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. Estimated photooxidation lifetime.

c. Hydrolysis rate is a minimum rate.

d. Half-lives are on the order of several minutes to a few hours, depending on the degree of agitation in the system; the range of values stated was determined under conditions of continuous mechanical stirring at 200 rpm.

42.6 Literature Cited

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43. 1,1-DICHLOROETHANE (ETHYLIDINE CHLORIDE)

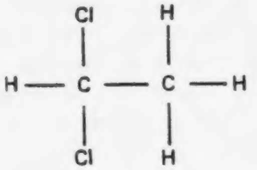
43.1 Statement of Probable Fate

Volatilization appears to be the major transport process for removal of 1,1-dichloroethane from aquatic systems. Once in the troposphere, 1,1-dichloroethane is attacked by hydroxyl radicals at a relatively rapid rate, so that the tropospheric lifetime is on the order of a month. A very small amount may reach the stratosphere, where it would undergo photodissociation. Very little information was found concerning other aquatic fate processes for this compound, but information on analogous compounds suggest that oxidation, hydrolysis and biodegradation are probably not important for 1,1-dichloroethane.

43.2 Identification

1,1-Dichloroethane, or ethylidine chloride, has been detected in finished drinking water by the National Organics Reconnaissance Survey (Environmental Protection Agency 1975a).

The chemical structure of 1,1-dichloroethane is shown below:



1,1-Dichloroethane

CAS NO. 75-34-3
TSL NO. KI 01750

Alternate Names

Ethylidene Chloride
Ethylidene Dichloride

43.3 Physical Properties

The general physical properties of 1,1-dichloroethane are given below.

Molecular weight (Weast 1977)	98.96
Melting point (Weast 1977)	-96.98°C
Boiling point at 760 torr (Weast 1977)	57.28°C

Vapor pressure at 20°C (Verschueren 1977)	180 torr
Solubility in water at 20°C (Verschueren 1977)	5,500 mg/l
Log octanol/water partition coefficient (Hansch *et al*. 1975)	1.79

43.4 Summary of Fate Data

43.4.1 Photolysis

No information pertaining specifically to the rate of photodissociation of 1,1-dichloroethane in the aqueous environment was found. Dilling *et al*. (1975) reported that within experimental error, sunlight did not accelerate the decomposition of dichloromethane, trichloromethane, and 1,1,1-trichloroethane (analogues of 1,1-dichloroethane) initially present at 1 mg/l concentrations in aerated water.

Photodissociation in the terrestrial environment would not be expected to occur for 1,1-dichloroethane since this compound has no chromophores which absorb in the visible or near ultraviolet region of the electromagnetic spectrum (Jaffé and Orchin 1962). The rate of reaction of 1,1-dichloroethane with hydroxyl radicals in the troposphere appears to be sufficiently rapid that very little of the unreacted compound will reach the stratosphere where it could undergo photodissociation due to the presence of higher energy, shorter wavelength ultraviolet light. Chloroacetyl chloride would probably be formed as the principal initial product of photodissociation (Environmental Protection Agency 1975b).

43.4.2 Oxidation

No information pertaining specifically to the oxidation of 1,1-dichloroethane in the aqueous environment was found. There is, however, indirect evidence that oxidation of this compound in aquatic systems is not important. Dilling *et al*. (1975) conducted aqueous reactivity experiments in which there was a large excess of dissolved oxygen compared to the total amount of dichloromethane, trichloromethane, and 1,1,1-trichloroethane, compounds similar to 1,1-dichloroethane. The half-lives for the three chloroalkanes in the system ranged from 6 to 18 months. The decomposition observed may have resulted from oxidation, hydrolysis, or both, but this range of half-lives is much longer than the 22 minute half-life reported by Dilling *et al*. (1975) for volatilization of 1,1-dichloroethane from a stirred aqueous system. In addition, the major portion of the disappearance was attributed to ionic hydrolysis rather than oxidation.

Due to the relatively high vapor pressure of 1,1-dichloroethane, volatilization to the atmosphere is expected to be quite rapid. Once in the troposphere, 1,1-dichloroethane is attacked by hydroxyl radicals. The biomolecular rate of this reaction at 23°C was found by Howard and Evenson (1976) to be $2.6(\pm 0.6)\times 10^{-13}\text{cm}^3\text{molecule}^{-1}\text{sec}^{-1}$, which, for a tropospheric hydroxyl radical concentration of 10^6cm^{-3}, corresponds to a lifetime (time for reduction to 1/e of original concentration) in the troposphere of about 1.5 months.

Based on a tropospheric lifetime of 1.5 months and a troposphere-to-stratosphere turnover time (time for all but 1/e of tropospheric air to diffuse into the stratosphere) of 30 years, somewhat less than one percent of tropospheric 1,1-dichloroethane would be expected to eventually reach the stratosphere. It should be noted that this estimation neglects the effects of 1,1-dichloroethane removal from the troposphere by other processes such as rainfall.

43.4.3 Hydrolysis

No information pertaining specifically to the hydrolytic half-life of 1,1-dichloroethane in the aqueous environment was found. Information on compounds structurally similar to 1,1-dichloroethane is not suitable for prediction of analogous behavior for this compound as is shown below:

Compound	Estimate of Hydrolytic Half-Life	Limitation	Reference
chloroethane	40 days	upper limit	Radding *et al*.(1977)
1,2-dichloroethane	50,000 years	upper limit	Radding *et al*.(1977)
1,1,1-trichloroethane	6 months	lower limit	Dilling *et al*.(1975)

In view of the volatility of 1,1-dichloroethane, however, it appears unlikely that hydrolysis would be the principal fate process for 1,1-dichloroethane.

43.4.4 Volatilization

Dilling *et al*. (1975) estimated the experimental half-life for volatilization of 1,1-dichloroethane originally present at 1 mg/l to be 22 minutes when stirred at 200 rpm in water at approximately 25°C in an open container. Removal of 90 percent of the 1,1-dichloroethane under the same conditions required 109 minutes. For chloroaliphatics in general, stirring speed was found to have a marked effect on volatilization rate. With intermittent stirring for 15 seconds every five minutes, the time required for 50 percent depletion of dichloromethane, trichloromethane and 1,1,1-trichloroethane, (compounds analogous to 1,1-dichloroethane) was greater than 90 minutes, or on the order of four times greater than was observed during constant stirring. The presence of sodium chloride at a 3 percent concentration, as in seawater, caused about a 10 percent decrease in the evaporative rate.

Dilling et al. (1975) are careful to point out the difficulties encountered in extrapolating their laboratory results to real-world conditions, where the concentration of the organic solute would probably be very much less than 1 mg/l and where surface and bulk agitation would be highly variable. Although the data appear to be valid on a relative basis (i.e., correctly illustrating the relative rates of volatilization of chlorinated aliphatics), they cannot be used as absolute measures of volatilization rates from natural waters. For the purposes of this document, the data are used as rough-order-of-magnitude indications of the importance of volatilization relative to other transport and fate processes, with the strong effects of agitation considered. The validity of this application has not been established.

A subsequent study by Dilling (1977) was conducted using the same experimental conditions as in the 1975 study, and an average half-life of 32.2 minutes was obtained for 1,1-dichloroethane at an initial concentration of 1 mg/l. The purpose of this subsequent study was to use the experimental data previously obtained to test two theoretical models which may be used to predict evaporative rates of slightly soluble organic compounds from water. Dilling (1977) found that the theoretical model proposed by Mackay and Wolkoff (1973) failed to predict evaporative half-lives, and that the theoretical model of Mackay and Leinonen (1975) using parameters of Liss and Slater (1974) correlated well with the experimental half-lives obtained. For example, the evaporative half-life obtained experimentally by Dilling (1977) was approximately 32 minutes as compared to a 21.2 minute evaporative half-life obtained by the Mackay and Leinonen (1975) model and 0.98 minutes predicted by the Mackay and Wolkoff (1973) model.

Dilling (1977), however, comments that the apparent numerical agreement between his data and the values predicted by the Mackay and Leinonen (1975) model may be fortuitous. Estimates of volatilization rates based on the Mackay and Leinonen (1975) model depend primarily on liquid-gas phase exchange rate constants, whereas the experimental model of Dilling et al. (1975) and Dilling (1977) is controlled by the rate of stirring and the wind velocity across the surface of the water.

Pearson and McConnell (1975) suggest that the presence of 1,2-dichloroethane (a structural isomer of 1,1-dichloroethane) and other halogenated aliphatics in ambient waters is due to the absorption of chloroorganics from the atmosphere by water and return to the earth during precipitation. Aerial transport of these chloroorganics is indicated by Pearson and McConnell (1975) to play a major role in the wider distribution of these compounds and accounts for their presence in upland waters.

43.4.5 Sorption

No information pertaining specifically to the adsorption of 1,1-dichloroethane onto sediments was found. Dilling et al. (1975) carried out two closed system experiments on dichloromethane, trichloromethane, and 1,1,1-trichloroethane, analogues of 1,1-dichloroethane, where solute loss could only occur by adsorption. Dry bentonite clay at 375 mg/l was introduced into a solution in a sealed container, and after ten minutes approximately ten percent of the chloroalkanes studied had been removed from solution, presumably through adsorption by the clay. When the amount of clay added to the closed system was doubled (750 mg/l) there was 22 percent solute loss after 30 minutes. There was no further solute adsorption after this time. Little selectivity was found among the various chlorinated compounds in the adsorption process. The authors observed some adsorption of dichloromethane, trichloromethane, and 1,1,1-tichloroethane by dry powdered dolomitic limestone, but, again, without selectivity among the solutes used.

In sealed aqueous samples that contained approximately 500 mg/l peat moss, approximately 40 percent of dichloromethane, trichloromoethane, and 1,1,1-trichloroethane was removed in 10 minutes (Dilling et al. 1975). At longer times, no further solute removal was noted.

Pearson and McConnell (1975) found no clear evidence of selective concentration of 1,1,1-trichloroethane, trichloromethane, and tetrachloromethane in sediments. Similar observations would presumably be obtained for 1,1-dichloroethane.

43.4.6 Bioaccumulation

According to Kopperman et al. (1976) not all organochlorine compounds bioaccumulate to high levels. The data suggest that polar compounds are more easily biodegraded, and the non-polar (highly lipophilic) compounds accumulate. Neely et al. (1974) have shown that bioaccumulation is related to the octanol/water partition coefficient (P) of the compound. The log octanol/water partition coefficient (log P) of 1.79 as calculated by the method of Hansch (Tute 1971; Hansch et al. 1975) indicates that 1,1-dichloroethane will probably not bioaccumulate to any significant extent (see Methods section on bioaccumulation).

43.4.7 Biotransformation and Biodegradation

No information pertaining specifically to the rate of biodegradation of 1,1-dichloroethane in aquatic systems was found. Thom and Agg (1975) have included 1,2-dichloroethane, an analogue of 1,1-dichloroethane, in a list of synthetic organic chemicals which should be degradable by biological sewage treatment provided suitable acclimatization can be achieved. They note, however, that not many compounds in this list occur in nature and, as a result, it is unlikely that microorganisms already possess the ability to destroy them. The authors consider 1,2-dichloroethane, along with various other compounds, to be potentially biodegradable. By analogy, 1,1-dichloroethane may also be potentially biodgradable.

According to Pearson and McConnell (1975) only completely sealed systems, such as the standard BOD (biochemical oxygen demand) bottle technique, can be used to measure biochemical degradation of volatile compounds such as 1,1-dichloroethane. The BOD bottle experiments of Pearson and McConnell have been unable to demonstrate any significant oxygen absorption from compounds containing only C, H, and Cl, thus indicating that biochemical degradation of such compounds is indeed very slow. Literature references to microbial biodegradation are few and conflicting; the majority indicate that low molecular weight chloroaliphatics are not metabolized (Pearson and McConnell 1975; McConnell et al. 1975).

Pearson and McConnell (1975) found some evidence of metabolism of 1,2-dichloroethane, an analogue of 1,1-dichloroethane, in the tissues of both fish and oysters. The administration of carbon-14 labeled 1,2-dichloroethane to fish and oysters resulted in rapid accumulation of ^{14}C to an asymptotic level, followed by loss on transfer to clean sea water. Analysis by gas chromatography, however, showed much lower levels of 1,2-dichloroethane to be present than predicted by the ^{14}C in the tissue, thus indicating that some metabolism may have occurred. It is possible that 1,1-dichloroethane may be metabolized as well.

43.5 Data Summary

Table 43-1 summarizes the aquatic fate information discussed above. The oxidation rate is a photooxidation rate for the reaction of 1,1-dichloroethane with hydroxyl radicals in the troposphere as well as the hydrosphere. 1,1-Dichloroethane is believed to be volatilized from aquatic systems rapidly, and subsequently to be photooxidized by hydroxyl radicals in the troposphere. The little information found concerning other fate processes indicate that they play a minor role in comparison to photooxidation for this compound.

Table 43-1

Summary of Aquatic Fate of 1,1-Dichloroethane

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Probably does not undergo significant photodissociation in the aquatic environment or in the atmosphere below the ozone layer.	-	-	Medium
Oxidation[a]	Photooxidation in the troposphere may be the predominant fate of this compound; photooxidation in the aquatic environment probably occurs at a slow rate; direct oxidation at ambient conditions probably does not significantly occur in the aquatic or atmospheric environment.	$2.6 \times 10^{-13} cm^3 molecule^{-1} sec^{-1}$	1.5 months[b]	Medium
Hydrolysis	Probably occurs too slowly to be a significant fate process.	-	-	Low
Volatilization	The primary transport process.	-	~20 to 30 minutes[c]	Medium
Sorption	Probably not important.	-	-	Low
Bioaccumulation	Probably does not significantly bioaccumulate.	-	-	Low
Biotransformation/ Biodegradation	There is evidence of metabolism of 1,2-dichloroethane, an analogue of 1,1-dichloroethane, by fish and oysters. 1,1-Dichloroethane may be metabolized, as well.	-	-	Low

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a. The predominant environmental process which is thought to determine the fate of the compound.

b. Estimated lifetime based on the rate constant.

c. Half-lives are on the order of several minutes to a few hours, depending on the degree of agitation in the system; the stated value was obtained under conditions of continual mechanical stirring at 200 rpm.

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44. 1,2-DICHLOROETHANE (ETHYLENE DICHLORIDE)

44.1 Statement of Probable Fate

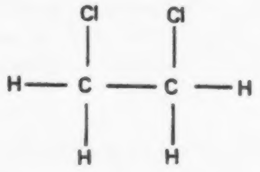
Volatilization appears to be the major transport process for removal of 1,2-dichloroethane from aquatic systems. Once in the troposphere, 1,2-dichloroethane is attacked by hydroxyl radicals, reportedly resulting in chloroacetyl chloride as the principal initial product. The atmospheric lifetime of 1,2-dichloroethane, based on its rate of reaction with hydroxyl radicals, is reported to be on the order of several months. Any unreacted 1,2-dichloroethane which diffuses upward to the stratosphere will undergo photodissociation.

Other processes do not appear to be significant for 1,2-dichloroethane. Oxidation in the aquatic environment probably does not occur except for limited photooxidation. Hydrolysis is also probably too slow to be an important process for removal of 1,2-dichloroethane. Although no information was found indicating that microorganisms exist which can readily biodegrade 1,2-dichloroethane, information was found to indicate that this compound may be metabolized by fish and oysters. There is, at present, no evidence of either bioaccumulation of 1,2-dichloroethane in aquatic organisms or adsorption of this compound onto suspended solids or sediments.

44.2 Identification

1,2-Dichloroethane, or ethylene dichloride, has been detected in finished drinking water by the National Organics Reconnaissance Survey (Environmental Protection Agency 1975a). In addition, 1,2-dichloroethane has been detected in the atmosphere in unquantified concentration (Hanst 1978).

The chemical structure of 1,2-dichloroethane is shown below.



1,2-Dichloroethane

CAS NO. 107-06-2
TSL NO. KI 05250

Alternate Names

Ethylene dichloride
Glycol dichloride

44.3 Physical Properties

The general physical properties of 1,2-dichloroethane are given below.

Molecular weight (Weast 1977)	98.98
Melting point (Weast 1977)	-35.36°C
Boiling point at 760 torr (Weast 1977)	83.47°C
Vapor pressure at 20°C (Verschueren 1977)	61 torr
Solubility in water at 20°C (Verschueren 1977)	8,690 mg/l
Log octanol/water partition coefficient (Radding *et al*. 1977)	1.48

44.4 Summary of Fate Data

44.4.1 Photolysis

No information pertaining specifically to the rate of photodissociation of 1,2-dichloroethane in the aqueous environment was found. Dilling *et al*. (1975) reported that, within experimental error, sunlight did not accelerate the decomposition of such compounds as dichloromethane, trichloromethane, and 1,1,1-trichloroethane (analogues of 1,2-dichloroethane) initially present at 1 mg/l concentrations in aerated water. Photodissociation of 1,2-dichloroethane in the aquatic environment would not be expected to occur since this compound has no chromophores which absorb in the visible or near ultraviolet region of the electromagnetic spectrum (Jaffé and Orchin 1962).

The rate of reaction of 1,2-dichloroethane with tropospheric hydroxyl radicals is sufficiently rapid that very little unreacted compound would be expected to reach the stratosphere where it couuld undergo photodissociation due to the presence of higher energy, shorter wavelength ultraviolet light. Chloroacetyl chloride would probably be an initial photodissociation product (Environmental Protection Agency 1975b).

44.4.2 Oxidation

No information pertaining specifically to the oxidation of 1,2-dichloroethane in the aqueous environment was found. There is, however, some indirect evidence from which the lack of potential for oxidation in aquatic systems can be inferred. Dilling et al. (1975) conducted aqueous reactivity experiments in which there was a large excess of dissolved oxygen compared to the total amount of dichloromethane, trichloromethane, and 1,1,1-trichloroethane, compounds that are similar to 1,2-dichloroethane. The rates of disappearance observed for these compounds were much lower than rates of loss by volatilization from water reported by the same authors for 1,2-dichloroethane and for the three analogous compounds. In addition, Dilling et al. (1975) attributed the major portion of the observed disappearance to ionic hydrolysis rather than to oxidation. These results indicate that direct oxidation in aquatic systems is probably not important for 1,2-dichloroethane.

Due to the relatively high vapor pressure of 1,2-dichloroethane, volatilization to the atmosphere is expected to be quite rapid. Once in the troposphere, the compound reacts with hydroxyl radicals. According to Howard and Evenson (1976), the bimolecular rate for this reaction at 23°C is 2.2 ($\pm$ 0.5) x 10^{-13} cm^3 $molecule^{-1}$ sec^{-1}, which, assuming a tropospheric hydroxyl radical concentration of 10^6 cm^{-3}, corresponds to a lifetime (time for reduction to 1/e of original concentration) in the troposphere of about 1.7 months. Radding et al. (1977) indicate an atmospheric half-life for this photooxidation reaction of 234 hours (0.3 months), corresponding to a rate constant of 0.1 x 10^{-9} M^{-1} sec^{-1}.

Other information on the reaction of 1,2-dichloroethane with hydroxyl radicals indicate an atmospheric lifetime of three or four months (Environmental Protection Agency 1975b). Chloracetyl chloride is reported to be the principal initial reaction products formed. This compound is readily hydrolyzed to HCl and the corresponding carboxylic acid (Morrison and Boyd 1973).

Based on a tropospheric lifetime on the order of one month, and assuming a troposphere-to-atmosphere turnover time (time for all but 1/e of tropospheric air to diffuse into the stratosphere) of 30 years, somewhat less than one percent of tropospheric 1,2-dichloroethane would be expected to eventually reach the stratosphere. It should be noted that the above analysis neglects the effects of other tropospheric removal processes such as scrubbing by rain.

44.4.3 Hydrolysis

A maximum hydrolytic half-life of 50,000 years has been estimated for 1,2-dichloroethane at pH 7 and 25°C from experimental data at 100-150°C (Radding et al. 1977). This corresponds to a first-order rate constant for hydrolysis of 1,2-dichloroethane of approximately 5 x $10^{-13}sec^{-1}$ (Radding et al. 1977). This estimated half-life is based on the half-life of 1,2-dibromoethane which, being brominated rather than chlorinated, was theorized to be ten times as reactive as 1,2-dichloroethane. The validity of this estimation method has not been established. It must be noted that 50,000 years is much longer than indicated by the 6 to 18 month minimum hydrolytic half-lives for similar compounds (dichloromethane, trichloromethane, 1,1,1-trichloroethane) reported by Dilling *et al*. (1975). In addition, Radding *et al*. (1977) estimated the hydrolytic half-life of chloroethane, another compound similar to 1,1-dichloroethane, to be 40 days or less. While the rate of hydrolysis does not appear to be well established for 1,2-dichloroethane, it appears unlikely that hydrolysis is important for this compound in aquatic systems because of the rapidity of the volatilization loss.

44.4.4 Volatilization

Dilling *et al*. (1975) estimated the experimental half-life for volatilization of 1,2-dichloroethane originally present at 1 mg/l to be 29 minutes when stirred at 200 rpm in water at approximately 25°C in an open container. Removal of 90 percent of the 1,2-dichloroethane under the same conditions required 96 minutes. For chloroaliphatics in general, stirring speed was found to have a marked effect on volatilization rate. With intermittent stirring for 15 seconds every five minutes, the time required for 50 percent depletion of dichloromethane, trichloromethane, and 1,1,1-trichloroethane, analogues of 1,2-dichloroethane, was greater than 90 minutes, or on the order of four times greater than was observed during constant stirring. The presence of sodium chloride at a 3 percent concentration, as in seawater, effected a 10 percent decrease in the evaporative rate of the chlorinated compound. Dilling *et al*. (1975) are careful to point out the difficulties encountered in extrapolating their laboratory results to real-world conditions, where the concentration of the organic solute would probably be very much less than 1 mg/l and where surface and bulk agitation would be highly variable. Although the data appear to be valid on a relative basis (i.e., correctly illustrating the relative rates of volatilization of chlorinated aliphatics), they cannot be used as absolute measures of volatilization rates from natural waters. For purposes of this document, the data are used as rough-order-of-magnitude indications of the importance of volatilization relative to other transport and fate processes, with the strong effects of agitation considered. The validity of this application has not been established.

A subsequent study by Dilling (1977) was conducted using the same experimental conditions as the aforementioned investigation, and an average half-life of 28 minutes with respect to volatilization of 1 mg/l of 1,2-dichloroethane was obtained. The purpose of this subsequent study was to use the experimental data obtained to test two theoretical models formulated to predict evaporative rates of slightly soluble organic compounds from water. Dilling (1977) found that the theoretical model by Mackay and Wolkoff (1973) failed to predict evaporative half-lives, but that the theoretical model of Mackay and Leinonen (1975) using parameters of Liss and Slater (1974) correlated well with the experimental half-lives obtained. For example, the evaporative half-life obtained experimentally by Dilling (1977) was approximately 28 minutes as compared to a 24.5 minute evaporative half-life obtained by the Mackay and Leinonen (1975) model, whereas the Mackay and Wolkoff (1973) model predicted a half-life of 4.5 minutes.

Dilling (1977) however, comments that the apparent numerical agreement between data and the values predicted by the Mackay and Leinonen (1975) model may be fortuitous. Estimates of volatilization rates based on the Mackay and Leinonen (1975) model depend primarily on liquid-gas phase exchange rate constants, whereas the experimental model of Dilling et al. (1975) and Dilling (1977) is controlled by the rate of stirring and the wind velocity across the surface of the water.

Pearson and McConnell (1975) suggest that the presence of 1,2-dichloroethane, as well as other halogenated aliphatics, in ambient waters is due to the absorption of chloroorganics from the atmosphere by water and their return to the earth in precipitation. Aerial transport of these chloroorganics is indicated by Pearson and McConnell (1975) to play a major role in their distribution and accounts for their presence in upland waters.

44.4.5 Sorption

No information pertaining specifically to the adsorption of 1,2-dichloroethane onto sediments was found. Dilling et al. (1975) carried out two closed system experiments on dichloromethane, trichloromethane, and 1,1,1-trichloroethane (analogues of 1,2-dichloroethane) where solute loss could occur by adsorption. Dry bentonite clay at 375 mg/l was introduced into a sealed solution of the haloaliphatic compounds and, after ten minutes, approximately ten percent of the initial solute was removed from solution, presumably through adsorption by the clay. When the amount of clay added to the closed system was doubled (750 mg/l), a solute loss of 22 percent occurred after 30 minutes with no further solute adsorption after this time. The authors indicated that there appeared to be little selectivity among the various chlorinated compounds in the adsorption process. Some adsorption of dichloromethane, trichloromethane, and 1,1,1-trichloroethane by dry powdered dolomitic limestone was also noted, but, again, without any selectivity among the compounds.

In sealed aqueous samples with approximately 500 mg/l peat moss, approximately 40 percent of chloroaliphatic solutes (dichloromethane, trichloromethane, and 1,1,1-trichloroethane) was removed in 10 minutes. At longer times, no further solute removal was noted.

Pearson and McConnell (1975) found no clear evidence of selective concentration of three analogues of 1,2-dichloroethane (1,1,1-trichloroethane, trichloromethane, and tetrachloromethane) in sediments. This would presumably also be the case for 1,2-dichloroethane.

44.4.6 Bioaccumulation

According to Kopperman et al. (1976) not all organochlorine compounds bioaccumulate to high levels. The data suggest that polar compounds are more easily biodegraded and that the non-polar (highly lipophilic) compounds accumulate. Neely et al. (1974) have shown that bioaccumulation is related to the octanol/water partition coefficient (P) of the compound. The log octanol/water partition coefficient (log P) of 1.48 (Radding et al. 1977) indicates that 1,2-dichloroethane will probably not bioaccumulate to any significant extent.

44.4.7 Biotransformation and Biodegradation

No information pertaining specifically to the rate of biodegradation of 1,2-dichloroethane in aquatic systems was found. Thom and Agg (1975) have included 1,2-dichloroethane in a list of synthetic organic chemicals which should be degradable by biological sewage treatment provided that suitable acclimatization can be achieved. They note, however, that not many compounds in this list occur in nature and, as a result, it is unlikely that microorganisms already possess the ability to destroy them.

According to Pearson and McConnell (1975) only completely sealed systems, such as the standard BOD (biochemical oxygen demand) bottle technique, can be used to measure biochemical degradation of volatile compounds such as 1,2-dichloroethane. The BOD bottle experiments of Pearson and McConnell have been unable to demonstrate any significant oxygen demand for compounds containing only C, H, and Cl, thus indicating that biochemical degradation of such compounds is indeed very slow. Literature references to microbial biodegradation are few and conflicting; the majority report that low molecular weight chloroaliphatics are not metabolized (Pearson and McConnell 1975; McConnell et al. 1975).

Pearson and McConnell (1975) found some evidence of metabolism of 1,2-dichloroethane in the tissues of both fish and oysters. The administration of carbon-14 labelled 1,2-dichloroethane to fish and oysters resulted in rapid accumulation of ^{14}C to an asymptotic level, followed by loss on transfer to clean sea water. Analysis by gas chromatography, however, showed much lower levels of 1,2-dichloroethane to be present than predicted by the ^{14}C accumulation, thus indicating that some metabolism may have occurred.

44.5 Data Summary

Table 44-1 summarizes the aquatic fate information discussed above. The oxidation rate is a photooxidation rate and refers to the rate of reaction of 1,2-dichloroethane with hydroxyl radicals in the troposphere as well as in the hydrosphere.

Due to the relatively high vapor pressure of 1,2-dichloroethane, volatilization from the aquatic system to the atmosphere is quite rapid. Once in the troposphere, 1,2-dichloroethane is photooxidized relatively rapidly, having an atmospheric lifetime of order one to four months. The photooxidation process appears to be much more rapid than other fate processes which could occur.

Table 44-1

Summary of Aquatic Fate of 1,2-Dichloroethane

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Appears to be insignificant in the aquatic environment; the slow photooxidation in the atmosphere probably leaves some unreacted compound to diffuse upward above the ozone layer to undergo photodissociation.	-	-	Medium
Oxidation[a]	Photooxidation in the troposphere appears to be the predominant fate of this compound; photooxidation in the aquatic environment occurs at a slow rate; direct oxidation at ambient conditions does not occur significantly in the aquatic or atmospheric environment.	$0.1 \times 10^{-9} M^{-1} sec^{-1}$[c] $2.2 \times 10^{-13} cm^3 molecule^{-1} sec^{-1}$	3 to 4 months[b] 234 hours[c] 1.7 months[d]	Medium
Hydrolysis	Probably occurs too slowly to be a significant fate process.	$\sim 5 \times 10^{-13} sec^{-1}$[e]	~50,000 years[e]	Low
Volatilization	The primary transport process.	-	~28 minutes[f]	Medium
Sorption	Probably not important.	-	-	Low
Bioaccumulation	Probably does not significantly bioaccumulate.	-	-	Low
Biotransformation/ Biodegradation	There is evidence of metabolism of 1,2-dichloroethane by fish and oysters.	-	-	Low

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a. The predominant environmental process which is thought to determine the fate of the compound.
b. Reported as an atmospheric lifetime of 3 to 4 months.
c. Reported as a half-life and rate constant for reaction of hydroxyl radical with 1,2-dichloroethane in the atmosphere.
d. Estimated tropospheric lifetime.
e. Hydrolysis rate is a minimum rate; the half-life indicates maximum persistence.
f. Half-lives are on the order of several minutes to a few hours; this half-life is based on experimental results of Dilling (1977) and Dilling et al. (1975) using a system agitated by stirring.

44.6 Literature Cited

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45. 1,1,1-TRICHLOROETHANE (METHYL CHLOROFORM)

45.1 Statement of Probable Fate

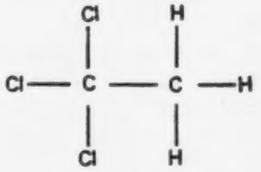
Volatilization is the major transport process for removal of 1,1,1-trichloroethane from aquatic systems. Once in the troposphere, 1,1,1-trichloroethane reacts with hydroxyl radicals. The principal tropospheric photooxidation product of 1,1,1-trichloroethane is reported to be trichloroacetaldehyde which is probably subsequently oxidized to trichloroacetic acid. This acid, as well as some unreacted 1,1,1-trichloroethane, could be washed out of the troposphere via precipitation. A portion of the unreacted 1,1,1-trichloroethane probably diffuses to the stratosphere where it undergoes photoodissociation by higher energy ultraviolet light with the subsequent formation of chlorine atoms and chlorine oxides.

Based on the information found, it does not appear that either oxidation or hydrolysis is an important fate process of 1,1,1-trichloroethane in the aquatic environment. Evidence concerning the importance of adsorption, bioaccumulation, and biodegradation is not definitive.

45.2 Identification

1,1,1-Trichloroethane is known to be ubiquitous in the environment. This compound has been detected in the atmosphere (Singh et al. 1978; Pearson and McConnell 1975), in finished drinking water (Environmental Protection Agency 1975a) in freshwater, rainwater, seawater, marine sediments (Pearson and McConnell 1975), marine organisms (Pearson and McConnell 1975; Dickson and Riley 1976), and in surface snow in Alaska (Su and Goldberg 1976).

The chemical structure of 1,1,1-trichloroethane is shown below.



1,1,1-Trichloroethane

CAS NO. 71-55-6
TSL NO. KJ 29750

Alternate Names

Methyl chloroform
Chlorotene
Genklene
Baltana

45.3 Physical Properties

The general physical properties of 1,1,1-trichloroethane are given below.

Molecular weight (Weast 1977)	133.41
Melting point (Weast 1977)	-30.41°C
Boiling point at 760 torr (Weast 1977)	74.1°C
Vapor pressure at 20°C (Pearson and McConnell 1975)	96.0 torr
Solubility in water at 20°C	480 to 4400 mg/l*
Log octanol/water partition coefficient (Calculated from Tute 1971, See Methods Section on bioaccumulation)	2.17

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*Several values for solubility of 1,1,1-trichloroethane in water at 20°C were found in the literature. These values range from 480 mg/l (Pearson and McConnell 1975) to 4400 mg/l (Verschueren 1977).

45.4 Summary of Fate Data

45.4.1 Photolysis

There was little information found pertaining specifically to the rate of photolysis of 1,1,1-trichloroethane in the aqueous environment. Dilling et al. (1975) studied the rate of photolysis of 1,1,1-trichloroethane at a concentration of 1 mg/l in aerated water in sealed tubes and found no significant difference between samples exposed to sunlight and those kept in the dark. Based on these results photolysis of 1,1,1-trichloroethane in the aqueous environment under ambient conditons does not appear to be a significant fate process.

Photodissociation in the water or the troposphere would not be expected to occur for 1,1,1-trichloroethane since this compound has no chromophores which absorb in the visible or near ultraviolet region of the electromagnetic spectrum (Jaffé and Orchin 1962).

Due to the high vapor pressure of 1,1,1-trichloroethane, volatilization to the atmosphere is quite rapid. 1,1,1-Trichloroethane has been described as relatively stable in the troposphere (McConnell and Schiff 1978; Hanst 1978; Lillian *et al.* 1975). However, it appears likely that most of the material entering the troposphere will be photooxidized by reaction with hydroxyl radicals, even though the rates reported are relatively slow in comparison with those for structurally similar chlorinated aliphatics. McConnell and Schiff (1978) report that approximately fifteen percent of the 1,1,1-trichloroethane discharged to the troposphere will be transported to the stratosphere where it will be rapidly photodissociated due to the presence of shorter wavelength, higher energy ultraviolet light. Chlorine atoms and chlorine oxides are reported to be the photodissociation products.

45.4.2 Oxidation

The literature reviewed indicates that oxidation probably does not play a significant role in the aquatic fate of 1,1,1-trichloroethane. Dilling *et al.* (1975) conducted laboratory experiments in which there was about a sixfold molar excess of dissolved oxygen compared to the total amount of 1,1,1-trichloroethane. Thus, there was a great excess of oxygen present which would have been available for complete oxidation of all the chlorinated compounds present. The results indicated that oxidation was very slow and, if it occurred at all, was much slower than volatilization.

Many tropospheric half-lives, lifetimes, and rate constants for 1,1,1-trichloroethane have been reported in the literature. Yung *et al.* (1975) have reported a bimolecular rate constant for 1,1,1-trichloroethane of $8.2 \times 10^{-13} cm^3 molecule^{-1} sec^{-1}$, corresponding to a maximum tropospheric lifetime (time required for reduction to 1/e of original concentration) of 9.5×10^7 seconds (approximately 3.1 years). McConnell and Schiff (1978) have reported a tropospheric lifetime of approximately 8 years based on a tropospheric hydroxyl radical concentration of $5 \times 10^5 cm^{-3}$. Watson *et al.* (1977) report a tropospheric lifetime of 4.39 years based on a weighted average temperature for the troposphere of 265°K and a global seasonally and diurnally averaged hydroxyl radical concentration of $9 \times 10^5 cm^{-3}$. In addition, Watson *et al.* (1977) report a bimolecular rate constant for reaction of hydroxyl radicals in the troposphere with 1,1,1-trichloroethane of $(1.59 \pm 0.16) \times 10^{-14} cm^3 sec^{-1}$ at 298°K. A tropospheric lifetime for 1,1,1-trichloroethane of 1.1 years has been reported by Cox *et al.* (1976), based on a bimolecular rate of reaction with hydroxyl radicals of $2.8 \times 10^{-14} cm^3 sec^{-1}$. This value agrees with the rate constant of $2.8 x 10^{-14} cm^3 molecule^{-1} sec^{-1}$ reported by Howard and Evenson (1976). A document by the Environmental Protection Agency (1975c) reports a tropospheric half-life of 1,1,1-trichloroethane of 1.1 years; the rate of reaction on which this half-life was based was not given, but may well have been taken from Cox *et al.* (1976) or Howard and Evenson (1976).

Photooxidation products for 1,1,1-trichloroethane have been reported in the literature. Christiansen et al. (1972) report the photooxidation products of 1,1,1-trichloroethane to be hydrogen chloride, carbon oxides, phosgene and, to a lesser extent, acetyl chloride. Both phosgene and acetyl chloride are readily hydrolyzed (Morrison and Boyd (1973). On the other hand, a document by the Environmental Protection Agency (1975c) reports that the principal tropospheric photooxidation product of 1,1,1-trichloroethane is trichloroacetaldehyde. According to the Environmental Protection Agency (1975c), it seems likely that trichloroacetaldehyde will subsequently be oxidized to trichloroacetic acid. This acid, once formed, could be washed out of the troposphere by precipitation (Environ-mental Protection Agency 1975c).

45.4.3 Hydrolysis

According to the Environmental Protection Agency (1975b) 1,1,1-trichloroethane is sensitive to hydrolysis. In addition, it is reported that 1,1,1-trichloroethane is easily hydrolyzed in an excess of free water especially at elevated temperatures and in the gas phase (Environmental Protection Agency 1975b). In citing the works of other authors, Dilling et al. (1975) reported that 1,1,1-trichloroethane is hydrolyzed at elevated temperatures with the formation of acetic and hydrochloric acids along with a minor amount of vinylidene chloride. Laboratory experiments by Dilling et al. (1975) were conducted in closed systems in the dark to eliminate some of the potentially competing processes such as evaporation, photolysis, and oxidation. The experimental half-life obtained was approximately six months at 25°C, corresponding to a first-order rate of 0.12 months^{-1} (Dilling et al. 1975). This may be considered a maximum rate for hydrolysis, although other processes might have been occurring.

45.4.4 Volatilization

Dilling et al. (1975) estimated the experimental half-life for volatilization of 1,1,1-trichloroethane originally present at 1 mg/l to be 20±3 minutes (average of three) when stirred at 200 rpm in water at approximately 25°C in an open container. Removal of 90 percent of the 1,1,1-trichloroethane under the same conditions required about 69 minutes (average of three). For chloroaliphatics in general, stirring speed was found to have a marked effect on volatilization rate. With intermittent stirring for 15 seconds every 5 minutes, the time required for 50 percent depletion of 1,1,1-trichloroethane was approximately 90 minutes, or on the order of four times greater than was observed during constant stirring. The presence of sodium chloride at a 3 percent concentration, as in seawater, caused about a ten percent decrease in the chlorinated compound evaporation rate.

Evaporation appears to be the major pathway by which 1,1,1-trichloroethane is lost from water. Dilling et al. (1975) are careful to point out the difficulties encountered in extrapolating their laboratory results to real-world conditions, where the concentration of the organic solute would probably be very much less than 1 mg/l and where surface and bulk agitation would be highly variable. Although the data appear to be valid on a relative basis (i.e., correctly illustrating the relative rates of volatilization of chlorinated aliphatics), they cannot be used as absolute measures of volatilization rates from natural waters. For the purposes of this document, the data are used as rough-order-of-magnitude indications of the importance of volatilization relative to other transport and fate processes, with the strong effects of agitation considered. The validity of this application has not been established.

A subsequent study by Dilling (1977) was conducted using the same experimental conditions as in the 1975 study, and an average evaporation half-life of 24.9 minutes was obtained for 0.97 mg/l 1,1,1-trichloroethane. The purpose of this subsequent study was to use the experimental data obtained to test two theoretical models formulated to predict evaporation rates of slightly soluble organic compounds from water. Dilling (1977) found that the theoretical model by Mackay and Wolkoff (1973) failed to predict evaporation half-lives, whereas the theoretical model of Mackay and Leinonen (1975), using parameters from Liss and Slater (1974), correlated well with the experimental half-lives obtained by Dilling (1977). For example, the evaporation half-life obtained experimentally by Dilling (1977) for 1,1,1-trichloroethane was approximately 17 to 25 minutes, in agreement with the evaporation half-life obtained by the Mackay and Leinonen (1975) model of 23.7 minutes, but very diffent from the value of 0.19 minutes predicted by the Mackay and Wolkoff (1973) model.

Dilling (1977), however, comments that the apparent numerical agreement between his data and the values predicted by the Mackay and Leinonen (1975) model may be fortuitous. Estimates of volatilization rates based on the Mackay and Leinonen (1975) model depend primarily on liquid-gas phase exchange rate constants, whereas the experimental model of Dilling et al. (1975) and Dilling (1977) is controlled by the rate of stirring and the wind velocity across the surface of the water.

In a study by Pearson and McConnell (1975), rainwater collected in Runcorn, England contained up to 9 x 10^{-11} parts (by mass) of 1,1,1-trichloroethane. Municipal waters supplied to the cities of Liverpool, Chester, and Manchester (all supplied from upland surface sources), contained up to 3 x 10^{-10} (by mass) tetrachloromethane plus 1,1,1-trichloroethane. While entry to the general environment appears to be predominantly evaporative, there may also be some chloroaliphatics in aqueous industrial effluents which will pass into municipal drainage and systems and rivers. Mackay and Wolkoff (1973) have shown that the evaporation rate of poorly soluble species from water can be quite high due to their high activity coefficients. Pearson and McConnell (1975) and McConnell et al. (1975) point out that this is a reversible process since water will absorb chloro-organics from the atmosphere, a process which will occur most effectively when the atmosphere is scrubbed during periods of rainfall. The presence of trace organochlorines, including 1,1,1-trichloroethane, in upland waters is believed to be due to aerial transport (Pearson and McConnell 1975; McConnell et al. 1975).

45.4.5 Sorption

Dilling et al. (1975) carried out two closed system experiments where solute loss could only be by adsorption. Dry bentonite clay at 375 mg/l was introduced into a sealed solution and in ten minutes there was approximately a ten percent adsorption of 1,1,1-trichloroethane, as well as other chlorinated compounds, by the clay compared to a blank. When the amount of clay added to the closed system was doubled (750 mg/l) there was 22 percent solute adsorption after 30 minutes. There was no further solute adsorption after this time. The authors indicated that there appeared to be little selectivity among the various chlorinated compounds in the adsorption process. The authors observed some adsorption of 1,1,1-trichloroethane by dry powdered dolomitic limestone, but, again, no selectivity among solutes was found.

In a sealed system with approximately 500 mg/l peat moss, approximately 40 percent of the 1,1,1-trichloroethane was adsorbed in 10 minutes. At longer times, no further solute removal was noted. The subsequent decrease in the rate of disappearance of 1,1,1-trichloroethane at time periods longer than 10 minutes was suggested to be due to gradual release or desorption of 1,1,1-trichloroethane from the peat moss to the solution.

Pearson and McConnell (1975) found that the concentrations of chloroorganics in Liverpool Bay sediments varied from a few ng/l to a maximum of 5500 ng/l of 1,1,1-trichloroethane plus tetrachloromethane combined. Samples of marine sediment from Liverpool Bay contained the same compounds as the overlying waters. Due to the inability of the analytical technique used to resolve tetrachloromethane and 1,1,1-trichloroethane, however, it could not be determined whether a correlation existed between the concentration of 1,1,1-trichloroethane in marine sediments and the concentration in the interstitial water at the time the samples were taken (Pearson and McConnell 1975; McConnell et al. 1975). In addition, it is unknown whether a correlation existed between high concentrations and geographical features, as was noticed in the case of water samples for several compounds, or whether there was a relationship between the concentration in the sediment and particle size. McConnell et al. (1975), however, did note that coarse gravels had little adsorptive capacity for

1,1,1-trichloroethane, whereas sediments rich in organic detritus had a much higher adsorptive capacity. In summary, there was no clear evidence of selective concentration of 1,1,1-trichloroethane in sediments.

45.4.6 Bioaccumulation

According to Kopperman *et al*. (1976) not all organochlorine compounds bioaccumulate to high levels. The data suggest that polar compounds are more easily biodegraded, whereas non-polar highly lipophilic compounds accumulate. Neely *et al*. (1974) have shown that bioaccumulation is directly related to the octanol/water partition coefficient (P) of the compound. The log octanol/water partition coefficient (log P) as determined by calculation using the method of Tute (1971) is 2.17 for 1,1,1-trichloroethane, indicating that bioaccumulation in the adipose tissues of organisms is possible, but that bioaccumulation is probably not an important transport mechanism for this compound.

Pearson and McConnell (1975) attempted to determine the level of 1,1,1-trichloroethane and other chlorinated hydrocarbons in the tissues of a wide range of organisms. Species were chosen to represent significant trophic levels in the marine environment. 1,1,1-Trichloroethane was well distributed, but due to difficulties with analytical methods, no reliable estimates of bioaccumulation could be made.

45.4.7 Biotransformation and Biodegradation

No information was found pertaining specifically to the rate of biodegradation of 1,1,1-trichloroethane in aquatic systems. Thom and Agg (1975) have included 1,1,1-trichloroethane in a list of synthetic organic chemicals which should be degradable by biological sewage treatment provided suitable acclimatization can be achieved. They note, however, that not many compounds in this list occur free in nature and, as a result, it is unlikely that microorganisms already possess the ability to destroy them.

According to Pearson and McConnell (1975) only completely sealed systems, such as the standard BOD (biochemical oxygen demand) bottle technique, can be used to measure biochemical degradation of volatile compounds such as 1,1,1-trichloroethane. The BOD bottle experiments of Pearson and McConnell have been unable to demonstrate any significant oxygen absorption from compounds containing only C, H, and Cl, thus indicating that biochemical degradation of such compounds is indeed very slow.

45.5 Data Summary

Table 45-1 summarizes the aquatic fate discussed above. The oxidation rate is a photooxidation rate and refers to the rate of reaction of 1,1,1-trichloroethane with hydroxyl radicals in the troposphere.

Due to the high vapor pressure of 1,1,1-trichloroethane, volatilization to the atmosphere is quite rapid. Although reaction with hydroxyl radicals in the troposphere is relatively slow, this photooxidation reaction appears to be the predominant fate process for the compound. The unreacted portion of tropospheric 1,1,1-trichloroethane returns to the earth via precipitation or diffuses to the stratosphere where it undergoes photodissociation as a result of the shorter wavelength, higher energy ultraviolet light present above the ozone layer. 1,1,1-Trichloroethane reaching the lithosphere via precipitation or dry fallout would be expected to evaporate readily.

Table 45-1

Summary of Aquatic Fate of 1,1,1-Trichloroethane

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Probably not significant in aquatic systems. Photodissociation in the stratosphere appears to be important for this compound.	-	-	Medium
Oxidation[a]	Not a significant fate process for this compound in aquatic systems; photooxidation in the troposphere is the predominant fate process.	from 8.2×10^{-13} $cm^3 sec^{-1}$ to 2.8×10^{-14} $cm^3 sec^{-1}$	from 1.1 years[b] to 8 years	High
Hydrolysis	Probably occurs too slowly to be a significant fate process.	0.12 $month^{-1}$[c]	6 months	Medium
Volatilization	The primary transport process from the aquatic environment.	-	~20-25 minutes[d]	Medium
Sorption	Probably not important.	-	-	Low
Bioaccumulation	Probably not important.	-	-	Low
Biotransformation/ Biodegradation	Probably occurs at an extremely slow rate.	-	-	Low

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a. The predominant environmental process which is thought to determine the fate of the compound.
b. Reported as lifetimes (time for reduction to 1/e of original concentration) of 1.1 to 8 years.
c. Should be considered as a maximum rate.
d. Half-lives are on the order of several minutes to a few hours, depending on the degree of agitation; the reported rate was determined in a stirred system.

45.6 Literature Cited

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46. 1,1,2-TRICHLOROETHANE

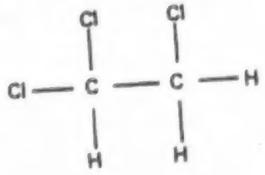
46.1 Statement of Probable Fate

Although only a relatively small amount of information pertaining specifically to 1,1,2-trichloroethane was found, the processes important to the fate of this compound in the environment can be inferred from information available on its more thoroughly studied structural isomer, 1,1,1-trichloroethane, and from available information on short-chain halogenated aliphatics in general. By analogy to 1,1,1-trichloroethane, photooxidation in the troposphere would be expected to be the predominant fate process for 1,1,2-trichloroethane. This, in turn, is contingent upon volatilization as the primary transport mechanism for removal of the compound from water.

46.2 Identification

1,1,2-Trichloroethane has been detected in finished drinking water by the National Organics Reconnaissance Survey (Environmental Protection Agency 1975).

The chemical structure of 1,1,2-trichloroethane is shown below.



1,1,2-Trichloroethane

CAS NO. 79-00-5
TSL NO. KJ 31500

Alternate Names

Vinyl trichloride

46.3 Physical Properties

The general physical properties of 1,1,2-trichloroethane are as follows.

Molecular weight (Weast 1977)	133.41
Melting point (Weast 1977)	-36.5°C
Boiling point at 760 torr (Weast 1977)	133.77°C

Vapor pressure at 20°C (Verschueren 1977)	19 torr
Solubility in water at 20°C (Verschueren 1977)	4,500 mg/l
Log octanol/water partition coefficient (Calculated from Tute (1971); see Methods Section on Bioaccumulation).	2.17

46.4 Summary of Fate Data

46.4.1 Photolysis

Relatively little information was found pertaining specifically to the rate of photolysis of 1,1,2-trichloroethane in the aquatic environment. Jensen and Rosenberg (1975), using a closed system wherein no evaporation could occur, found no significant difference between 1,1,2-trichloroethane in the closed system in daylight and 1,1,2-trichloroethane in the closed system in darkness, thus indicating that little or no photodissociation occurred. Both seawater and deionized and boiled fresh water were utilized in these tests. Dilling *et al*. (1975) reported that, within experimental error, sunlight did not accelerate decomposition of 1,1,1-trichloroethane, a structural isomer of 1,1,2-trichloroethane, initially present at a concentration of 1 mg/l in aerated water.

Photodissociation in the terrestrial environment would not be expected to occur for 1,1,2-trichloroethane since this compound has no chromophores which absorb in the visible or near ultraviolet region of the electromagnetic spectrum (Jaffé and Orchin 1962). In the stratosphere, however, 1,1,2-trichloroethane would be expected to be photodissociated due to the presence of shorter wavelength, higher energy ultraviolet light.

46.4.2 Oxidation

No information pertaining specifically to the oxidation of 1,1,2-trichloroethane in the aquatic environment was found. There is, however, some indirect evidence that oxidation in aquatic systems is not important. For instance, Dilling *et al*. (1975) conducted aqueous reactivity experiments in which there was a large excess of dissolved oxygen compared to the total amount of 1,1,1-trichloroethane. The results indicated that volatilization was much more rapid than any oxidative process which may have occurred.

Once in the troposphere, 1,1,2-trichloroethane would be expected to react with hydroxyl radicals. This photooxidation reaction should proceed at a rate intermediate between those for 1,2-dichloroethane and 1,1,1-trichloroethane, two structurally similar compounds, because of the comparative number and placement of the chlorine atoms on the three compounds. Based on the data of Howard and Evenson (1976) the tropospheric lifetime (time for reduction to 1/e of original concentration), of 1,2-dichloroethane, as a result of reaction with hydroxyl radicals, is on the order of one to several months, while the troposphere half-life for 1,1,1-trichloroethane is reported to be on the order of a few years (McConnell and Schiff 1978; Hanst 1978; Lillian et al. 1975).

Assuming an upper limit on the tropospheric lifetime for 1,1,2-trichloroethane of three years, and a troposphere-to-stratosphere turnover time (time for all but 1/e of tropospheric air to diffuse into the stratosphere) of 30 years, less than ten percent of the 1,1,2-trichloroethane would be expected to reach the stratosphere. It thus appears that photooxidation in the troposphere is much more important than stratospheric photodissociation for this compound.

46.4.3 Hydrolysis

No information pertaining specifically to the rate of hydrolysis of 1,1,2-trichloroethane in the environment was found. Dilling et al. (1975) conducted laboratory experiments in closed systems in the dark to eliminate competing processes such as evaporation and photolysis. The experimental hydrolytic half-life obtained for 1,1,1-trichloroethane, a structural isomer of 1,1,2-trichloroethane, was approximately six months at 25°C (Dilling et al. 1975). This corresponds to a first-order rate of 0.12 months^{-1} (Dilling et al. 1975) which should be considered a maximum rate for hydrolysis. By analogy 1,1,2-trichloroethane may be expected to undergo hydrolysis at a rate on the same order, that is, about 0.1 month^{-1}.

46.4.4 Volatilization

Dilling et al. (1975) estimated the experimental half-life for volatilization of 1,1,2-trichloroethane originally present at 1 mg/l to be 21 minutes when stirred at 200 rpm in water at approximately 25°C in an open container. Removal of 90 percent of the 1,1,2-trichloroethane under the same conditions required 102 minutes. For chloroaliphatics in general, stirring speed was found to have a marked effect on volatilization rate. When intermittent stirring of 15 seconds duration was provided every five minutes, the time required for 50 percent depletion of 1,1,1-trichloroethane, a structural isomer of 1,1,2-trichloroethane, was greater than 90 minutes. This half-life is on the order of four times longer than for evaporation with constant stirring. The presence of sodium chloride at a 3 percent concentration, as in seawater, caused a 10 percent decrease in the rate of evaporation.

Dilling et al. (1975) are careful to point out the difficulties encountered in extrapolating their laboratory results to real-world conditions, where the concentration of the organic solute would probably be very much less than 1 mg/l and where surface and bulk agitation would be highly variable. Although the data appear to be valid on a relative basis (i.e., correctly illustrating the relative rates of volatilization of chlorinated aliphatics), they cannot be used as absolute measures of volatilization rates from natural waters. For the purposes of this document, the data are used as rough-order-of-magnitude indications of the importance of volatilization relative to other transport and fate proceses, with the strong effects of agitation considered. The validity of this application has not been established.

A subsequent study by Dilling (1977) was conducted using the same experimental conditions as in the 1975 study, and an average evaportion half-life of 35.1 minutes was obtained for 1,1,2-trichloroethane initially present at a concentration of 0.99 mg/l. The purpose of this subsequent study was to use the experimental data previously obtained to test two theoretical models which may be used to predict evaportive rates of slightly soluble organic compounds from water. Dilling (1977) found that the theoretical model of Mackay and Wolkoff (1973) failed to predict evaporative half-lives, but that the model of Mackay and Leinonen (1975) using the parameters of Liss and Slater (1974) correlated well with the experimental half-lives obtained. For example, the evaporative half-life obtained experimentally by Dilling (1977) was approximately 35 minutes, compared to 30.1 minutes predicted by the Mackay and Leinonen (1975) model and 6.1 minutes predicted by the Mackay and Wolkoff (1973) model.

Dilling (1977), however, comments that the apparent numerical agreement between his data and the values predicted by the Mackay and Leinonen (1975) model may be fortuitous. Estimates of volatilization rates based on the Mackay and Leinonen (1975) model depend primarily on liquid-gas phase exchange rate constants, whereas the experimental model of Dilling et al. (1975) and Dilling (1977) is controlled by the rate of stirring and the wind velocity across the surface of the water.

Pearson and McConnell (1975) suggest that the presence of compounds similar to 1,1,2-trichloroethane (1,1,1-trichloroethane and others) in ambient waters is due to the absorption of these compounds from the atmosphere by water, particularly during precipitation. Aerial transport of halogenated aliphatics in general is indicated by Pearson and McConnell (1975) to play a major role in the wider distribution of these compounds and accounts for their presence in upland waters.

46.4.5 Sorption

No information was found pertaining specifically to the adsorption of 1,1,2-trichloroethane onto sediments. Dilling et al. (1975) carried out two closed system experiments on approximately 1 mg/l of 1,1,1-trichloroethane (a structural isomer of 1,1,2-trichloroethane) where solute loss could only be by adsorption. Dry bentonite clay at 375 mg/l was introduced into a sealed solution and in ten minutes there was approximately a ten percent adsorption of the solute by the clay. When the amount of clay added to the closed system was doubled (750 mg/l) there was 22 percent solute adsorption after 30 minutes but no further solute adsorption after this time. The authors indicated that there appeared to be little selectivity among the various chlorinated compounds in the adsorption process. The authors observed some adsorption of 1,1,1-trichloroethane by dry powdered dolomitic limestone, but, again, without any selectivity among the compounds used.

In the sealed system with approximately 500 mg/l peat moss, approximately 40 percent of 1,1,1-trichloroethane was adsorbed in 10 minutes. At longer times, no further solute removal was noted. The subsequent decrease in the rate of disappearance of 1,1,1-trichloroethane at longer time periods than 10 minutes was suggested to be due to gradual release of 1,1,1-trichloroethane from the peat moss to the solution.

Pearson and McConnell (1975) found no clear evidence of selective concentrations of 1,1,1-trichloroethane in sediments; because of structural similarities, 1,1,2-trichloroethane should behave similarly.

46.4.6 Bioaccumulation

According to Kopperman et al. (1976) not all organochlorine compounds bioaccumulate to high levels. The data suggest that polar compounds are more easily biodegraded, and the non-polar (highly lipophilic) compounds accumulate. Neely et al. (1974) have shown that bioaccumulation is related to the octanol/water partition coefficient (P) of the compound. The log octanol/water partition coefficient (log P) of 2.17 as calculated by the method of Hansch (Tute 1971) indicates that 1,1,2-trichloroethane will probably not bioaccumulate to any significant extent (See Methods section on Bioaccumulation).

46.4.7 Biotransformation and Biodegradation

No information pertaining specifically to the rate of biodegradation of 1,1,2-trichloroethane in aquatic systems was found. Pearson and McConnell (1975) stated that only completely sealed systems, such as the standard BOD (biochemical oxygen demand) bottle technique, can be used to measure biochemical degradation of volatile compounds such as 1,1,2-trichloromethane. The BOD bottle experiments of Pearson and McConnell have been unable to demonstrate any significant oxygen absorption from compounds containing only C, H, and Cl, thus indicating that biochemical degradation of such compounds is indeed very slow. Literature references to microbial biodegradation of low molecular weight chloroaliphatics are few and conflicting; the majority find that these compounds are not metabolized (Pearson and McConnell 1975; McConnell *et al*. 1975).

46.5 Data Summary

Table 46-1 summarizes the aquatic fate information discussed above. The information found pertaining specifically to 1,1,2-trichloroethane is relatively scant. Based on the specific information found and information inferred by analogy to 1,1,1-trichloroethane, one can predict with low confidence that the predominant fate of 1,1,2-trichloroethane is photooxidation in the troposphere. This fate is, of course, contingent upon volatilization as the dominant transport process for removal of 1,1,2-trichloroethane from aquatic systems.

Table 46-1

Summary of Aquatic Fate of 1,1,2-Trichloroethane

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Probably not significant in aquatic systems; photodissociation in the stratosphere may be a significant fate of this compound.	-	-	Low
Oxidation[a]	Not a significant fate process for this compound in aquatic systems; tropospheric photooxidation probably is the predominant fate process.	-	-	Low
Hydrolysis	Probably occurs too slowly to be a significant fate process.	-	-	Low
Volatilization	Although the vapor pressure of this compound is somewhat lower than for 1,1,1-trichloroethane, volatilization probably serves as the primary transport process.	-	~20 to 35 minutes[b]	Medium
Sorption	Data are inconclusive.	-	-	-
Bioaccumulation	Data are inconclusive.	-	-	-
Biotransformation/ Biodegradation	Probably occurs at a slow rate.	-	-	Low

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a. The predominant environmental process which is thought to determine the fate of the compound.

b. Half-lives are on the order of several minutes to a few hours, depending on the degree of agitation in the system. The range given was reported by Dilling (1977) and Dilling et al. (1975) at conditions of constant 200 rpm stirring.

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47. 1,1,2,2-TETRACHLOROETHANE

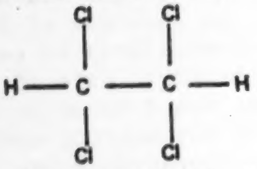
47.1 Statement of Probable Fate

Little information pertaining specifically to the environmental fate of 1,1,2,2-tetrachloroethane was found. By analogy to a more thoroughly studied analogue, 1,1,1-trichloroethane, both photooxidation in the troposphere and photodissociation in the stratosphere may be important fate processes for 1,1,2,2-tetrachloroethane. The importance of these processes in comparison to fate processes in aqueous media depends, in turn, on volatilization as the major process for removal from aquatic systems. Although volatilization appears to be relatively rapid, essentially no information was found concerning possibly competing processes.

47.2 Identification

1,1,2,2-Tetrachloroethane has been detected in finished drinking water (Shackelford and Keith 1976).

The chemical structure of 1,1,2,2-tetrachloroethane is shown below.



1,1,2,2-Tetrachloroethane

CAS NO. 79-34-5
TSL NO. KI 85750

Alternate Names

sym-Tetrachloroethane
Acetylene tetrachloride

47.3 Physical Properties

The general physical properties of 1,1,2,2-tetrachloroethane are as follows.

Molecular weight (Weast 1977)	167.85
Melting point (Weast 1977)	-36°C
Boiling point at 760 torr (Weast 1977)	146.2°C

Vapor pressure at 20°C (Verschueren 1977)	5 torr
Solubility in water at 20°C (Verschueren 1977)	2,900 mg/l
Log octanol/water partition coefficient (Calculated from Tute 1971; see Methods section on Bioaccumulation)	2.56

47.4 Summary of Fate Data

47.4.1 Photolysis

Relatively little information pertaining specifically to the rate of photolysis of 1,1,2,2-tetrachloroethane in the aquatic environment was found. Jensen and Rosenberg (1975), using a closed system in which no evaporation could occur, found no significant difference between 1,1,2,2-tetrachloroethane depletion in the closed system in daylight and in darkness, thus indicating that no significant photolysis occurred. Dilling *et al*. (1975) reported that, within experimental error, sunlight did not accelerate decomposition of 1,1,1-trichloroethane, an analogue of 1,1,2,2-tetrachloroethane, initially present at 1 mg/l concentrations in aerated water. It is thus not possible to determine whether photolysis of either 1,1,1,-trichloroethane or 1,1,2,2-tetrachloroethane would occur in water at a significant rate. Moreover, photodissociation in the aquatic environment would not be expected to occur since 1,1,2,2-tetrachloroethane has no chromophores which absorb in the visible or near ultraviolet region of the electromagnetic spectrum (Jaffé and Orchin 1962). In the stratosphere, however, 1,1,2,2-tetrachloroethane would be expected to react analogously to 1,1,1-trichloroethane and be photodissociated by high energy ultraviolet light.

47.4.2 Oxidation

No information pertaining specifically to the oxidation of 1,1,2,2-tetrachloroethane in the aquatic environment was found. There is, however, some indirect evidence for the lack of a potential for oxidation of this compound in aquatic systems. Dilling *et al*. (1975) conducted experiments in aqueous solutions where there was a large excess of dissolved oxygen compared to the total amount of 1,1,1-trichloroethane, an analogue of 1,1,2,2-tetrachloroethane. The results indicated that the 1,1,1-trichloroethane was relatively stable under the oxidative conditions used, exhibiting a combined half-life with respect to both oxidation and hydrolysis of 6 months. Dilling *et al*. (1975) attribute the decomposition observed to hydrolysis rather than oxidative processes.

Once in the troposphere 1,1,2,2-tetrachloroethane would be expected to undergo a photooxidation reaction with hydroxyl radicals. The tropospheric half-life of 1,1,1-trichloroethane, a structurally similar compound, is reported to be on the order of a few years (McConnell and Schiff 1978; Hanst 1978; Lillian _et al_. 1975), and McConnell and Schiff (1978) estimate that 15 percent of tropospheric 1,1,1-trichloroethane may reach the stratosphere where it can be photodissociated. If the rate of tropospheric photooxidation for 1,1,2,2-tetrachloroethane is similar to that of 1,1,1-trichloroehane, then it appears that both tropospheric photooxidation and photodissociation in the stratosphere are probably important fate processes for 1,1,2,2-tetrachloroethane. Because of the lack of data specific to 1,1,2,2-tetrachloroethane, however, the relative importance of these two processes cannot be determined.

47.4.3 Hydrolysis

No information pertaining specifically to the rate of hydrolysis of 1,1,2,2-tetrachloroethane in the environment was found. In the reactivity experiments of Dilling _et al_. (1975) in which light was excluded from closed systems, the experimental half-life obtained for 1,1,1-trichloroethane, an analogue of 1,1,2,2-tetrachloroethane, was approximately six months at 25°C. The decomposition was primarily attributed to hydrolysis. This half-life corresponds to a first-order rate of 0.12 months^{-1} (Dilling _et al_. 1975), which is probably a maximum rate with respect to hydrolysis under environmental conditions. Analogously, 1,1,2,2-tetrachloroethane may be expected to undergo hydrolysis at a rate corresponding to a half-life of several months to a few years.

47.4.4 Volatilization

Dilling _et al_. (1975) estimated the experimental half-life for volatilization of 1,1,2,2-tetrachloroethane originally present at 1 mg/l to be 56 minutes when stirred at 200 rpm in water at approximately 25°C in an open container. Removal of 90 percent of the compound under the same conditions required over 120 minutes. For chloroaliphatics in general, stirring speed was found to have a marked effect on volatilization rate. When intermittent stirring of 15 seconds duration was provided every five minutes, the time required for 50 percent depletion of 1,1,1-trichloroethane, an analogue of 1,1,2,2-tetrachloroethane, was greater than 90 minutes, which was four times greater than evaporation with constant stirring for this compound. The presence of sodium chloride at a 3 percent concentration, as in seawater, caused a decrease in the rate of evaporation of short-chain chloroaliphatics. Dilling _et al_. (1975) are careful to point out the difficulties encountered in extrapolating their laboratory results to real-world conditions, where the concentration of the organic solute would probably be very much less than 1 mg/l and where surface and bulk agitation would be highly variable. Although the data appear to be valid on a relative basis (i.e., correctly illustrating the relative rates of volatilization of chlorinated aliphatics), they cannot be used as absolute measures of volatilization rates from natural waters. For the purposes of this document, the data are used as rough-order-of-magnitude indications of the importance of volatilization relative to other transport and fate proceses, with the strong effects of agitation considered. The validity of this application has not been established.

A subsequent study by Dilling (1977) was conducted using the same general experimental conditions as in the previous investigation, and an average half-life of 55.2 minutes was obtained for an initial concentration of 0.92 mg/l 1,1,2,2-tetrachloroethane in water. The purpose of this subsequent study was to use the experimental data previously obtained to test two theoretical models which may be used to predict evaporative rates of slightly soluble organic compounds from water. Dilling (1977) found that the theoretical model of Mackay and Wolkoff (1973) failed to predict evaporative half-lives, whereas the theoretical model of Mackay and Leinonen (1975) using the parameters of Liss and Slater (1974) correlated well with the experimental half-lives obtained by Dilling (1977). For example, the evaporative half-life obtained experimentally by Dilling (1977) was approximately 55 minutes, similar to a 40.5 minute evaporative half-life predicted by the Mackay and Leinonen (1975) model, but very different from the value of 12 minutes predicted by the Mackay and Wolkoff (1973) model.

Dilling (1977), however, comments that the apparent numerical agreement between his data and the values predicted by the Mackay and Leinonen (1975) model may be fortuitous. Estimates of volatilization rates based on the Mackay and Leinonen (1975) model depend primarily on liquid-gas phase exchange rate constants, whereas the experimental model of Dilling et al. (1975) and Dilling (1977) is controlled by the rate of stirring and the wind velocity across the surface of the water.

Pearson and McConnell (1975) suggest that the presence of 1,1,1-trichloroethane (an analogue of 1,1,2,2-tetrachloroethane) and other halogenated aliphatics in ambient waters is due to the absorption of these compounds from the atmosphere by water and return to the earth in precipitation. Aerial transport of halogenated aliphatics is indicated by Pearson and McConnell (1975) to play a major role in the wider distribution of these compounds and accounts for their presence in upland waters.

47.4.5 Sorption

No information pertaining specifically to the adsorption of 1,1,2,2-tetrachloroethane onto sediments was found. Dilling et al. (1975)

carried out two closed system experiments on 1,1,1-trichloroethane, an analogue of 1,1,2,2-tetrachloroethane, wherein solute loss could occur only by adsorption. Dry bentonite clay at 375 mg/l was introduced into a sealed solution, and in ten minutes approximately ten percent of solute was adsorbed by the clay. When the amount of clay added to the closed system was doubled (750 mg/l), there occurred 22 percent solute adsorption after 30 minutes, and no further solute adsorption after this time. The authors indicated that there appeared to be little selectivity among the various chlorinated compounds in the adsorption process. The authors also observed some adsorption of 1,1,1-trichloroethane by dry powdered dolomitic limestone, but, again, without any selectivity among the chloroaliphatics being studied. In the sealed system with approximately 500 mg/l peat moss, approximately 40 percent of 1,1,1-trichloroethane as a solute was adsorbed in 10 minutes. No further solute removal was noted upon further sampling.

Pearson and McConnell (1975) found no clear evidence of selective concentration of 1,1,1-trichloroethane in sediments. It is anticipated that observations under the same conditions for 1,1,2,2-tetrachloroethane would be similar to those reported above for 1,1,1-trichloroethane. However, these data are inconclusive as to the importance of sorption in the aquatic transport of 1,1,2,2-tetrachloroethane.

47.4.6 Bioaccumulation

According to Kopperman et al. (1976) not all organochlorine compounds bioaccumulate to high levels. The data suggest that polar compounds are more easily biodegraded, and the non-polar (highly lipophilic) compounds accumulate. Neely et al. (1974) have shown that bioaccumulation is related to the octanol/water partition coefficient (P) of the compound. The log octanol/water partition coefficient (log P) of 2.56 calculated by the method of Hansch (Tute 1971) indicates that bioaccumulation of 1,1,2,2-tetrachloroethane is possible (see Methods section on bioaccumulation), but its importance cannot be assessed at this time.

47.4.7 Biotransformation and Biodegradation

No information pertaining specifically to the rate of biodegradation of 1,1,2,2-tetrachloroethane in aquatic systems was found. According to Pearson and McConnell (1975), only completely sealed systems, such as the standard BOD (Biochemical Oxygen Demand) bottle technique, can be used to measure biochemical degradation of volatile compounds such as 1,1,2,2-tetrachloroethane. The BOD bottle experiments of Pearson and McConnell have been unable to demonstrate any significant oxygen absorption when compounds that contained only C, H, and Cl were being evaluated, thus indicating that biochemical degradation of such compounds is indeed very slow. Literature references to microbial biodegradation are few and conflicting; the majority find that low molecular weight chloroalilphatics are not metabolized (Pearson and McConnell 1975; McConnell et al. 1975).

47.5 Data Summary

Table 47-1 summarizes the aquatic fate information discussed above. The information found pertaining specifically to 1,1,2,2-tetrachloroethane is relatively scant. Based on the specific information found and information obtained by analogy to 1,1,1-trichloroethane and other halogenated aliphatic compounds, one can predict (with low confidence) that volatilization is the major transport process for removal from aquatic systems and that photooxidation in the troposphere and photodissociation in the stratosphere are each important fate processes. The predominante fate process cannot be predicted from the information presented.

Table 47-1

Summary of Aquatic Fate of 1,1,2,2-Tetrachloroethane

Environmental Process[a]	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Probably not significant in aquatic systems; photodissociation in the stratosphere is probably a significant fate process for this compound.	-	-	Low
Oxidation	Not a significant fate process for this compound in aquatic systems; photooxidation in the troposphere probably is important.	-	-	Low
Hydrolysis	Appears to occur too slowly to be a significant fate process.			Low
Volatilization	Since the vapor pressure of this compound is reasonably high, volatilization probably serves as the primary transport process.	-	∿55 minutes[b]	Low
Sorption	Data are inconclusive.	-	-	-
Bioaccumulation	Data are inconclusive.	-	-	-
Biotransformation/ Biodegradation	Probably occurs at a low rate, if at all.	-	-	Low

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. Half-lives are on the order of 55 minutes to several hours, depending on the degree of agitation in the system; the value stated is based on determinations made under conditions of continuous mechanical stirring at 200 rpm.

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48. HEXACHLOROETHANE

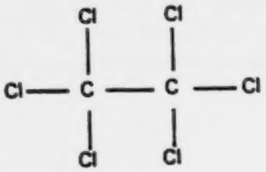
48.1 Statement of Probable Fate

Very little information pertaining specifically to the aquatic fate of hexachloroethane was found. It is, therefore, not possible to determine the aquatic fate of hexachloroethane at this time.

48.2 Identification

Hexachloroethane has been detected in finished drinking water (Shackelford and Keith 1976; Environmental Protection Agency 1975).

The chemical structure of hexachloroethane is shown below.



$$\mathrm{Cl_3C{-}CCl_3}$$

Hexachloroethane

CAS NO. 67-72-1
TSL NO. KI 40250

Alternate Names

Perchloroethane
Carbon hexachloride

48.3 Physical Properties

The general physical properties of hexachloroethane are given below.

Molecular weight (Weast 1977)	236.74
Melting point (Weast 1977)	Sublimes
Boiling point at 777 torr (Weast 1977)	186°C
Vapor pressure at 20°C (Verschueren 1977)	0.4 torr
Solubility in water at 22°C (Verschueren 1977)	50 mg/l
Log octanol/water partition coefficient (Calculated from Tute 1971; see Methods section on Bioaccumulation)	3.34

48.4 Summary of Fate Data

48.4.1 Photolysis

No specific information pertaining to the rate of photolysis of hexachloroethane in the aqueous environment under ambient conditions was found.

Photolysis in the atmosphere is important if hexachloroethane volatilizes appreciably; unfortunately, the relative importance of volatilization in comparison to other processes is unknown for this compound. In the event that a portion of the hexachloroethane should enter the atmosphere, it would be expected to behave as its more thoroughly studied analogue, tetrachloromethane. Tetrachloromethane is relatively stable in the troposphere with respect to reaction with hydroxyl radicals and does not directly photodissociate since it has no chromophores which absorb in the visible or near ultraviolet region of the electromagnetic spectrum (Jaffé and Orchin 1962). Like tetrachloromethane, some portion of hexachloroethane may diffuse unreacted to the stratosphere where significant photodissociation could occur.

48.4.2 Oxidation

No information was found pertaining specifically to the oxidation of hexachloroethane in the aquatic environment under ambient conditions. Hexachloroethane probably behaves similarly to other halogenated aliphatics in that it is not easily oxidized in aquatic systems since there are no functional groups present on the compound which react strongly with hydroxyl radicals (OH•).

No information was found pertaining specifically to the oxidation of hexachloroethane in the atmospheric environment under ambient conditions. Inferences can be made by analogy of hexachloroethane to tetrachloromethane; the reaction of tetrachloromethane with hydroxyl radicals in the troposphere, if it occurs, is very slow.

48.4.3 Hydrolysis

No information on hydrolysis of hexachloroethane was found.

48.4.4 Volatilization

Dilling *et al*. (1975) reported the experimental half-life with respect to volatilization of 1 mg/l hexachloroethane in water to be 45 minutes when stirred at 200 rpm at approximately 25°C in an open container. Removal of 90 percent hexachloroethane required greater than 120 minutes.

The stirring speed had a marked effect on the evaporative rate. With intermittent stirring for 15 seconds every 5 minutes, the time required for 50 percent depletion of 1,1,1-trichloroethane and trichloromethane, two analogues of hexachloroethane, was approximately 90 minutes or on the order of four times greater than was observed during constant stirring for these two compounds. The presence of sodium chloride at a 3 percent concentration, as in seawater, effected a ten percent decrease in evaporative rate for short-chain chloroaliphatics.

It is uncertain whether evaporation is the major pathway by which hexachloroethane is lost from water. Dilling *et al*. (1975) are careful to point out the difficulties encountered in extrapolating their laboratory results to real-world conditions, where the concentration of the organic solute would probably be very much less than 1 mg/l and where surface and bulk agitation would be highly variable. Although the data appear to be valid on a relative basis (i.e., correctly illustrating the relative rates of volatilization of chlorinated aliphatics), they cannot be used as absolute measures of volatilization rates from natural waters. For the purposes of this document, the data are used as rough-order-of-magnitude indications of the importance of volatilization relative to other transport and fate proceses, with the strong effects of agitation considered. The validity of this application has not been established.

A subsequent study by Dilling (1977) was conducted using similar experimental conditions as in the previous investigation, and an average evaporative half-life of 40.7 minutes was obtained for 0.72 mg/l hexachloroethane in stirred water.

The purpose of this subsequent study was to use the experimental data that was obtained to test two theoretical models formulated to predict evaporative rates of slightly soluble organic compounds from water. Dilling (1977) found that the theoretical model by Mackay and Wolkoff (1973) failed to predict evaporative half-lives, whereas the theoretical model of Mackay and Leinonen (1975) using the parameters of Liss and Slater (1974) correlated well with the experimental half-lives obtained by Dilling (1977). For example, the evaporative half-life of 40.7 minutes obtained experimentally by Dilling (1977) is in relatively close agreement with the evaporative half-life predicted by the Mackay and Leinonen model of 38 minutes but very different from the value of 4 minutes predicted by the Mackay and Wolkoff (1973) model.

Dilling (1977), however, comments that the apparent numerical agreement between his data and the values predicted by the Mackay and Leinonen (1975) model may be fortuitous. Estimates of volatilization rates based on the Mackay and Leinonen (1975) model depend primarily on liquid-gas phase exchange rate constants, whereas the experimental model of Dilling *et al*. (1975) and Dilling (1977) is controlled by the rate of stirring and the wind velocity across the surface of the water.

Pearson and McConnell (1975) theorize that the presence of organochlorine compounds in upland waters is a result of atmospheric transport and precipitation from the atmosphere by mechanisms such as rainfall and dew-like condensation.

48.4.5 Sorption

No information was found pertaining specifically to the adsorption of hexachloroethane. Pearson and McConnell (1975), however, have found other low molecular weight organochlorine compounds in Liverpool Bay (England) sediments at concentrations of a few nanograms per kilogram. Those compounds contained in the samples of marine sediment were the same as those compounds present in the overlying waters. There has been very little information published which indicates the presence of hexachloroethane in bodies of water, and no information was found concerning its existence in aquatic sediments.

48.4.6 Bioaccumulation

According to Kopperman *et al*. (1976), not all organochlorine compounds bioaccumulate to high levels. The data suggest that polar compounds are more easily biodegraded, whereas the non-polar (highly lipophilic) compounds accumulate. In addition, Neely *et al*. (1974) have theorized that bioaccumulation is directly related to the partition coefficient (P) of the compound. The log octanol/water partition coefficient (log P) of 3.34 calculated from Tute (1971) indicates that hexachloroethane may exhibit a tendency to bioaccumulate in organisms (see Methods section on bioaccumulation).

Significant bioaccumulation of hexachloroethane would require an absence of biodegradation and a large environmental loading. Not enough information was found to determine whether hexachloroethane might be present in the aquatic environment under these conditions.

48.4.7 Biotransformation and Biodegradation

No information was found pertaining specifically to the biodegradation of hexachloroethane. Literature references to microbial biodegradation are few and conflicting; the majority find that low molecular weight chloroaliphatics are not metabolized (Pearson and McConnell 1975; McConnell *et al*. 1975). Although Pearson and McConnell (1975) were unable to demonstrate microbial degradation of the chlorinated ethanes, they did observe the occurrence of chemical degradation of similar compounds.

48.5 Data Summary

Table 48-1 summarizes the aquatic fate information discussed above. Not enough information was found to predict the most likely aquatic fate of this compound.

Table 48-1

Summary of Aquatic Fate of Hexachloroethane

Environmental Process[a]	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Probably does not undergo photodissociation in the aquatic or lower atmospheric environments; stratosphere photodissociation may be important.	-	-	Low
Oxidation	Probably does not significantly oxidize in aquatic systems; if it is similar to its analogue tetrachloromethane, the atmospheric oxidation would be expected to be slow.	-	-	Low
Hydrolysis	No information found.	-	-	-
Volatilization	Evidence is inconclusive as to the relative importance of volatilization.	-	~40 to 45 minutes[b]	Low
Sorption	No specific information found.	-	-	-
Bioaccumulation	The high log octanol/water partition coefficient indicates that this compound may be bioaccumulated.	-	-	Low
Biotransformation/ Biodegradation	No specific information found.	-	-	-

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. Calculated and observed half-lives range up to several hours; this rate is based on the experimental results of Dilling (1977) and Dilling et al. (1975), in which mechanical stirring (200 rpm) was utilized.

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49. CHLOROETHENE (VINYL CHLORIDE)

49.1 Statement of Probable Fate

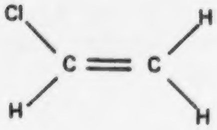
Chloroethene introduced into aquatic systems will most probably be quickly transferred to the atmosphere through volatilization. In fact, results from model simulations indicate that chloroethene should not remain in an aquatic ecosystem under most natural conditions. Once in the troposphere, chloroethene reacts at an extremely rapid rate with hydroxyl radicals, exhibiting a half-life on the order of a few hours with the subsequent formation of hydrogen chloride or formyl chloride as possible products. Formyl chloride, if formed, is reported to decompose thermally at ambient temperatures with a half-life of about 20 minutes, yielding carbon monoxide and hydrogen chloride. As a result, chloroethene in the troposphere should be decomposed within a day or two of release.

Based on the information found, it does not appear that oxidation, hydrolysis, and biodegradation are important fate processes for chloroethene in the aquatic environment, nor do sorption and bioaccumulation appear to be important transport processes.

49.2 Identification

Chloroethene has been detected in finished drinking water (Environmental Protection Agency 1975a), in the atmosphere (Environmental Protection Agency 1974; Lillian *et al*. 1975; Gay *et al*. 1976), and in industrial waterborne discharges (Environmental Protection Agency 1974).

The chemical structure of chloroethene is shown below.



Chloroethene

CAS NO. 75-01-4
TSL NO. KU 96250

Alternate Names

Vinyl chloride
Monochloroethylene
Monovinylchloride
MVC
Chloroethylene

49.3 Physical Properties

The general physical properties of chloroethene are given below.

Molecular weight (Weast 1977)	62.50
Melting point (Weast 1977)	-153.8°C
Boiling point at 760 torr (Weast 1977)	-13.37°C
Vapor pressure at 25°C (Verschueren 1977)	2,660 torr
Solubility in water at 10°C	
(Pearson and McConnell 1975)	60 mg/l
(Verschueren 1977)	1.1 mg/l at 25°C
Log octanol/water partition coefficient (Radding *et al*. 1977)	0.60

49.4 Summary of Fate Data

49.4.1 Photolysis

Atmospheric ozone prevents essentially all sunlight of wavelengths shorter than 290 nm from reaching the earth's surface. Chloroethene, in the vapor phase, does not absorb light of wavelengths greater than 220 nm, and in water it does not absorb above 218 nm (Hill *et al*. 1976). As a result, direct photolysis of chloroethene would be expected, at best, to be a very slow process due to lack of overlap between chloroethene absorption and sunlight radiation spectra. To confirm this experimentally, Hill *et al*. (1976) exposed solutions of 10 mg/l chloroethene in water to filtered light of greater than 300 nm from a mercury lamp. No photolysis occurred over a 90-hour period.

It is, however, possible that light-induced transformations of chloroethene could occur through indirect photolysis. Photolysis experiments were conducted by Hill *et al*. (1976) in natural water and in distilled water containing photosensitizers that absorb light of wavelengths greater than 300 nm. It was found that chloroethene in solution decomposed rapidly when irradiated with ultraviolet light in the presence of acetone, a high energy triplet sensitizer, or hydrogen peroxide, a free radical source. Photosensitization via energy transfer for the disappearance of chloroethene monomers occurs efficiently only when the triplet state energy of the sensitizer equals or exceeds that of the acceptor (which is, in this case, chloroethene monomer). Since the triplet state energies of monoolefins are very high (78-82 kcal $mole^{-1}$), only high energy sensitizers such as acetone (triplet energy 80 kcal $mole^{-1}$) are effective. Little is known, however, about the concentrations and distribution of high-energy sensitizers in the aquatic environment. Polyvinyl chloride plants are likely to use small amounts of peroxides in the polymerization process, and, as a result, sunlight-induced decomposition of chloroethene monomers is considered as a possible pathway for its disappearance from polyvinyl chloride plant effluent water (Hill et al. 1976).

Atmospheric photodissociation of chloroethene appears to be much less important than photochemical oxidation. Rapid photochemical oxidation is reported to remove the compound from the troposphere with a half-life of a few hours (Environmental Protection Agency 1975b). As a result, neither the chlorine in chloroethene nor chloroethene itself is likely to diffuse to the stratosphere.

49.4.2 Oxidation

Experiments at elevated temperatures (85°C) have shown that chloroethene is degraded in the presence of hydrogen peroxide, the chloroethene reacting with hydroxyl radicals (HO•) from peroxide decomposition (Hill et al. 1976). The decomposition of hydrogen peroxide is probably the rate determining step. The significance of this reaction pathway is difficult to assess because no data are available concerning the concentration and species of free radicals in natural waters. These experiments do indicate, however, that if reactive radicals are present in natural waters at significant concentrations, they may degrade chloroethene. Experimental results show that chloroethene will not be significantly degraded by molecular oxygen at temperatures and oxygen concentrations present in natural waters (Hill et al. 1976).

Chloroethene is tropospherically reactive and, as a result, will not accumulate in the troposphere (Environmental Protection Agency 1975b; Lillian et al. 1975). In the rapid photochemical oxidation reaction, chlorine is removed from the chloroethene with the subsequent formation of hydrogen chloride (HCl) or formyl chloride (HCOCl) as possible products (Environmental Protection Agency 1975b). Formyl chloride, if formed, is reported to decompose at room temperature with a half-life of about 20 minutes, yielding carbon monoxide (CO) and hydrogen chloride (HCl). As a result, almost all atmospheric chloroethene should be destroyed within a day or two of release. The hydrogen chloride formed is reported to be removed from the troposphere during precipitation.

49.4.3 Hydrolysis

Hydrolysis over a pH range of 4.3 to 9.4 does not appear to be an important pathway for loss of chloroethene from water (Environmental Protection Agency 1974). This statement is based on results obtained from studies of chloroethene levels in samples of clarifier effluent from a chloroethene plant stored at 50°C for 57 hours at pH 4.3, 8.0, and 9.4 in sealed septum vials. Concentrations of chloroethene remaining in these vials indicated that chloroethene decreased at the same rate at each pH condition (Environmental Protection Agency 1974). This lack of pH dependence indicates that chloroethene loss probably occurred due to volatilization rather than hydrolysis (Environmental Protection Agency 1974).

The hydrolytic half-life of chloroethene has been estimated to be less than 10 years at 25°C (Hill *et al*. 1976). Since the volatilization rate of chloroethene is much more rapid than the predicted rate of hydrolysis, hydrolysis should not be a significant aquatic fate.

49.4.4 Volatilization

Hill *et al*. (1976) indicate that loss of chloroethene from the aquatic environment by volatilization appears to be the most significant process affecting its distribution. This high rate of volatilization is due to the high vapor pressure (2,660 torr at 25°C) and the low solubility in water of 1.1 mg/l at 25°C (Verschueren 1977). On the basis of various model simulations formulated by Hill *et al*. (1976), it appears that chloroethene should not remain in an aquatic ecosystem under most natural conditions. The loss of chloroethene at constant temperature and pressure is a function of water turbulence and mixing efficiency (Hill *et al*. 1976).

Dilling *et al*. (1975) estimated the experimental half-life of volatilization of chloroethene originally present at 1 mg/l to be 26 minutes when stirred at 200 rpm in water at approximately 25°C in an open container. Removal of 90 percent of the chloroethene under the same conditions required 96 minutes. For chloroaliphatics in general, stirring speed was found to have a marked effect on volatilization rate.

Dilling *et al*. (1975) are careful to point out the difficulties encountered in extrapolating their laboratory results to real-world conditions, where the concentration of the organic solute would probably be very much less than 1 mg/l and where surface and bulk agitation would be highly variable. Although the data appear to be valid on a relative basis (i.e., correctly illustrating the relative rates of volatilization of chlorinated aliphatics), they cannot be used as absolute measures of volatilization rates from natural waters. For the purposes of this document, the data are used as rough-order-of-magnitude indications of the importance of volatilization relative to other transport and fate proceses, with the strong effects of agitation considered. The validity of this application has not been established.

A subsequent study by Dilling (1977) was conducted using the same experimental conditions as in the 1975 study, and a half-life of 27.6 minutes was obtained for 0.89 mg/l chloroethene in water. The purpose of this subsequent study was to use the experimental data to test two theoretical models used to predict evaporative rates of slightly soluble organic compounds from water. Dilling (1977) found that the model of Mackay and Wolkoff (1973) failed to predict evaporative half-lives, but that the model of Mackay and Leinonen (1975), using parameters from Liss and Slater (1974), correlated well with experimental results. For example, the evaporative half-life obtained experimentally by Dilling (1977) was approximately 28 minutes for chloroethene, as compared to 16.1 minutes predicted by the Mackay and Leinonen (1975) model and 0.0054 minutes predicted by the Mackay and Wolkoff (1973) model.

Dilling (1977), however, comments that the apparent numerical agreement between his data and the values predicted by the Mackay and Leinonen (1975) model may be fortuitous. Estimates of volatilization rates based on the Mackay and Leinonen (1975) model depend primarily on liquid-gas phase exchange rate constants, whereas the experimental model of Dilling *et al*. (1975) and Dilling (1977) is controlled by the rate of stirring and the wind velocity across the surface of the water.

The Environmental Protection Agency (1974) reported the experimental decrease of 16 mg/l chloroethene to be 96 percent in two hours when stirred rapidly at 22°C in an open beaker of distilled water. In contrast, quiescent water under the same conditions yielded a chloroethene concentration loss over two hours of only 25 percent (Environmental Protection Agency 1974).

Assuming that all processes involved are strictly first order, the volatilization loss data above (Environmental Protection Agency 1974) yields half-lives of 25.8 minutes for the stirred case and 290 minutes for the quiescent case. The half-life of 25.8 minutes for the stirred case agrees very closely with the 27.6 minute evaporative half-life with stirring reported by Dilling (1977). Volatilization rate data for chloroethene based on the above references can be summarized as follows:

Agitation	Evaporative Half-life (Minutes)
Rapid Continual Stirring	25.8
Continual Stirring at 200 rpm	27.6
Discontinuous Stirring (5% of the time)	~ 80-90
Quiescent; No Stirring	290

Hill et al. (1976) found that the rate of bulk exchange of gaseous chloroethene between atmosphere and water is about twice that of oxygen. As a result, Hill et al. (1976) conclude that the loss of chloroethene by volatilization from water is probably the most significant process in its distribution.

49.4.5 Sorption

There is little information pertaining specifically to the rate of adsorption of chloroethene onto particulate matter. In a study on the behavior of chloroethene in water, the Environmental Protection Agency (1974) found no significant difference in the rate of chloroethene loss from distilled water, river water, or effluent from a chloroethene plant stirred at the same rate, thus indicating negligible adsorption of chloroethene onto particulate matter. Hill et al. (1976) indicate that aquatic sediments could exhibit long-term storage of low levels of chloroethene if extreme environmental conditions, such as continual high levels of chloroethene input, were present.

49.4.6 Bioaccumulation

According to Kopperman et al. (1976), not all organochlorine compounds bioaccumulate to high levels. The data suggest that polar compounds are more easily biodegraded, whereas non-polar highly lipophilic compounds accumulate. Neely et al. (1974) have shown that bioaccumulation is directly related to the octanol/water partition coefficient (P) of the compound. The log octanol/water partition coefficient (log P) as reported in Radding et al. (1977) is 0.60, indicating little tendency for bioaccumulation in the adipose tissues of organisms.

Some authors (Lu et al. 1977; Environmental Protection Agency 1974) contend that chloroethene is too readily volatilized to undergo bioaccumulation, except perhaps in the most extreme exposure conditions. Studies by Hill et al. (1976) on five bacterial, three fungal, and two single organism cultures from natural aquatic systems did not show bioaccumulation to be an appreciable process.

49.4.7 Biotransformation and Biodegradation

Existing evidence indicates that chloroethene is resistant to microbial degradation. Studies by Hill et al. (1976) using an isolated bacterial culture containing two species of bacteria and three mixed fungal populations were unable to show that chloroethene was biodegraded over a five week period at concentrations of 20-120 mg/l.

49.4.8 Other Reactions

Hill et al. (1976) indicate that conditions could possibly exist where chloroethene could be converted to more highly chlorinated compounds. In environments such as municipal water chlorination facilities, high concentrations of chloride would exist. Under certain conditions, chloroethene may be converted to more highly chlorinated compounds based on the reactivity of carbon-carbon double bonds with chlorine and hypohalous acid.

Dissolved chloroethene in water will readily escape into the gas phase, but chemical reactions can occur with water impurities which may inhibit its release. Many salts have the ability to form complexes with chloroethene and can increase its solubility. Therefore, the amounts of chloroethene in water could be influenced significantly by the presence of salts (Environmental Protection Agency 1975c).

49.5 Data Summary

Table 49-1 summarizes the aquatic fate discussed above. Oxidation rates are photooxidation rates and refer to the rate of reaction of chloroethene with hydroxyl radicals in the troposphere.

Due to the high vapor pressure of chloroethene, volatilization to the atmosphere is quite rapid. In fact, from the results of model simulations it appears that chloroethene should not remain in an aquatic ecosystem under most natural conditions (Hill et al. 1976). Once in the troposphere, chloroethene reacts at an extremely rapid rate with hydroxyl radicals.

Table 49-1

Summary of Aquatic Fate of Chloroethene

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Not a significant fate process since photooxidation destroys chloroethene before it can reach the stratosphere, which is the region above the ozone layer where direct photolysis could occur.	-	-	High
Oxidation[a]	Photooxidation in the troposphere is the predominant fate of this compound; oxidation in the aquatic environment is probably not significant.	-	A few hours[b]	High
Hydrolysis	Probably not a significant fate of this compound.	-	<10 years	Medium
Volatilization	The most important transport process for vinyl chloride.	-	26 minutes[c]	High
Sorption	Probably not a significant transport process.	-	-	Medium
Bioaccumulation	Probably not a significant sink for this compound.	-	-	High
Biotransformation/ Biodegradation	Resistant to microbial degradation.	-	-	Medium

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a. The predominant environmental process which is thought to determine the fate of the compound.

b. This half-life is the reported half-life of chloroethene in the troposphere.

c. Half-lives are on the order of several minutes to a few hours; this half-life is based on a maximum rate of volatilization obtained from experiments in which the solutions were stirred rapidly.

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50. 1,1-DICHLOROETHENE (VINYLIDINE CHLORIDE)

50.1 Statement of Probable Fate

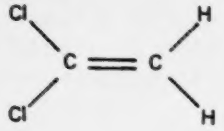
Volatilization appears to be the major transport process for removal of 1,1-dichloroethene from aquatic systems. Once in the troposphere, the compound is attacked by hydroxyl radicals at the double bond, reportedly resulting in such products as chloroacetyl chloride, phosgene, formic acid, hydrochloric acid, carbon monoxide, and formaldehyde. The tropospheric lifetime of 1,1-dichloroethene, based on its rate of reaction with hydroxyl radicals, appears to be substantially less than one day. This is an estimated lifetime extrapolated from the reported lifetime of trichloroethene, a more highly chlorinated analogue of 1,1-dichloroethene. Due to the projected reactivity of 1,1-dichloroethene with hydroxyl radicals in the troposphere, it is unlikely that unreacted 1,1-dichloroethene will reach the stratosphere.

Neither hydrolysis nor oxidation in the aquatic environment appears to be a significant fate process for 1,1-dichloroethene. No information was found indicating that microorganisms exist which can readily biodegrade 1,1-dichloroethene. In addition, no evidence of bioaccumulation of 1,1-dichloroethene in aquatic organisms or selective adsorption of this compound onto suspended sediments was found.

50.2 Identification

1,1-Dichloroethene, or vinylidene chloride, has been detected in finished drinking water (Environmental Protection Agency 1975a).

The chemical structure of 1,1-dichloroethene is shown below:



1,1-Dichloroethene

CAS NO. 75-35-4
TSL NO. KV 92750

Alternate Names

Vinylidene chloride
Vinylidine chloride
1,1-Dichloroethylene
1,1-DCE

50.3 Physical Properties

The general physical properties of 1,1-dichloroethene are given below:

Molecular weight (Weast 1977)	96.94
Melting point (Weast 1977)	-122.1°C
Boiling point at 760 torr (Weast 1977)	37°C
Vapor pressure at 25°C (Verschueren 1977)	591 torr
Solubility in water at 20°C (Pearson and McConnell 1975)	400 mg/l
Log octanol/water partition coefficient (Tute 1971; See Methods section on Bioaccumulation)	1.48

50.4 Summary of Fate Data

50.4.1 Photolysis

No information pertaining specifically to the rate of photodissociation of 1,1-dichloroethene in the aquatic environment was found. Jensen and Rosenberg (1975), using a closed system where no evaporation could occur, found no significant difference between samples stored in daylight and in darkness for tetrachloroethene and trichloroethene, two analogues of 1,1-dichloroethene. From these results, it was assumed that no significant photolysis occured for these two compounds and that similar results would be obtained for 1,1-dichloroethene.

1,1-Dichloroethene is quite volatile and, as a result, is rapidly transported to the troposphere. Photodissociation in water or in the troposphere would not be expected to occur for 1,1-dichloroethene since this compound has no chromophores which absorb in the visible or near ultraviolet region of the electromagnetic spectrum (Jaffé and Orchin 1962). In addition, 1,1-dichloroethene would not be expected to be available for photodissociation above the ozone layer because of rapid photooxidation in the troposphere.

50.4.2 Oxidation

No information pertaining specifically to the rate of oxidation of 1,1-dichloroethene in the aquatic environment was found. In a study utilizing closely related analogues, trichloroethene and tetrachloroethene, Dilling _et al_. (1975) conducted laboratory experiments in which there was about a sixfold molar excess of dissolved oxygen compared to the total amounts of trichloroethene and tetrachloroethene. The air space above the solutions in closed systems contained approximately 90 times as much oxygen as was present in the saturated solutions. Thus, there was a great excess of oxygen present which would have been available for complete oxidation of trichloroethene and tetrachloroethene. The experimental results indicate that volatilization is much more rapid than any oxidative process which may have occurred.

Dilling _et al_. (1975) did, however, find evidence of significant photooxidation of tetrachloroethene and trichloroethene in aqueous media in the presence of sunlight. The amounts of tetrachloroethene and trichloroethene remaining in aerated water in the dark after 12 months is approximately 13 and 20 percent greater, respectively, than the amount of tetrachloroethene and trichloroethene remaining in similar samples stored in the presence of sunlight. The finding that sunlight had a significant effect on the reactivity of tetrachloroethene and trichloroethene is consistent with predictions based on vapor phase photolysis studies showing that tetrachloroethene and trichloroethene disappeared when irradiated with long wavelength light in the presence of nitric oxide or nitrogen dioxide (Altshuller and Bufalini 1971). Dilling _et al_. (1975) attribute the difference in disappearance of tetrachloroethene and trichloroethene in the presence and absence of sunlight to free radical oxidation. It seems likely that 1,1-dichloroethene would also exhibit significant indirect photooxidation in aqueous media in the presence of sunlight since this compound is less chlorinated than tetrachloroethene and trichloroethene and, thus, would probably be even more amenable to attack at the double bond.

1,1-Dichloroethene is quite volatile and, thus, would be expected to be transported rapidly to the troposphere. Once in the troposphere, 1,1-dichloroethene should undergo fairly rapid photooxidation via hydroxyl radical attack on the double bond, in similar fashion to the photooxidation reported for tetrachloroethene and trichloroethene (Environmental Protection Agency 1975b). Gay _et al_. (1976) have reported that photooxidation of 1,1-dichloroethene is even more rapid than photooxidation of trichloroethene and tetrachloroethene under conditions of fairly constant halocarbon to NO_2 ratios. Gay _et al_. (1976) maintain that, since this ratio is approximately constant, the reactivities of the compounds studied are at least semi-quantitative. The greater reactivity of the less chlorinated alkanes is consistent with the results of Yung _et al_. (1975).

According to Dilling _et al_. (1976), 1,1-dichloroethene, cis-dichloroethene and trans-dichloroethene, trichloroethene and chloroethene decomposed at moderate rates when compared with a series of standard hydrocarbons such as ethene, trans-2-butene, and others under simulated atmospheric conditions. These compounds were reported by Dilling _et al_. (1976) to have estimated half-lives of 5 to 12 hours under bright sunlight in the presence of nitric oxide.

Pearson and McConnell (1975) exposed quartz flasks that contained air and small amounts of halogenated aliphatic compounds (10^{-7} to 10^{-4} by mass) to the diurnal and climatic variations of incident radiation and temperature. The air used for the experiment was not subjected to any pretreatment and was, thus, not identical in terms of its humidity or in its more detailed composition for all the experiments. Samples of air were withdrawn periodically for analysis of residual halogenated aliphatics. Half-lives for halogenated aliphatic compounds obtained by interpolation have a reproducibility of ±50% and are dependent on the climatic conditions prevailing at the time of the experiment. An interpolated tropospheric half-life of 8 weeks was obtained for 1,1-dichloroethene. This half-life, however, is probably not very accurate for two reasons. First, experiments were not set up and monitored simultaneously and, therefore, samples were not subject to the same changes of solar flux and temperature. Second, the quartz flasks were not filled with the same composition of air.

Gay _et al_. (1976) reported the photooxidation products of 1,1-dichloroethene to be chloroacetyl chloride, phosgene, formic acid, hydrochloric acid, carbon monoxide, and formaldehyde. Pearson and McConnell (1975) reported the photooxidation products of 1,1-dichloroethene irradiated in air by xenon arc (filtered to remove radiation of wavelengths below 290 nm) to be carbon monoxide, carbon dioxide, and hydrochloric acid. The lack of agreement between the products found by Gay _et al_. (1976) and Pearson and McConnell (1975) may be due to differences in experimental conditions.

50.4.3 Hydrolysis

No information pertaining specifically to the rate of hydrolysis of 1,1-dichloroethene in the aquatic environment was found. A study of two closely related analogues, trichloroethene and tetrachloroethene was included in work by Dilling _et al_. (1975) who conducted reactivity experiments in closed aqueous systems in the absence of light to eliminate competing processes such as volatilization and photolysis. The experimental half-lives obtained for tetrachloroethene and trichloroethene were 8.8 and 10.7 months, respectively. In terms of hydrolysis, these values can, at best, be regarded only as maximum half-lives, since the relative contributions of hydrolysis and oxidation in the experiments cannot be ascertained.

50.4.4 Volatilization

Dilling et al. (1975) estimated the experimental half-life for volatilization of 1,1-dichloroethene originally present at 1 mg/l to be 22 minutes when stirred at 200 rpm in water at approximately 25°C in an open container. Removal of 90 percent of the 1,1-dichloroethene under the same conditions required 89 minutes. For chloroaliphatics in general, stirring speed was found to have a marked effect on volatilization rate. With intermittent stirring for 15 seconds every five minutes, the time required for 50 percent depletion of tetrachloroethene and trichloroethene, analogues of 1,1-dichloroethene, was greater than 90 minutes, or four times greater than was observed for these compounds during constant stirring. The presence of sodium chloride at a 3 percent concentration, as in seawater, caused about a 10 percent decrease in the chlorinated compound evaporation rate. Dilling et al. (1975) are careful to point out the difficulties encountered in extrapolating their laboratory results to real-world conditions, where the concentration of the organic solute would probably be very much less than 1 mg/l and where surface and bulk agitation would be highly variable. Although the data appear to be valid on a relative basis (i.e., correctly illustrating the relative rates of volatilization of chlorinated aliphatics), they cannot be used as absolute measures of volatilization rates from natural waters. For the purposes of this document, the data are used as rough-order-of-magnitude indications of the importance of volatilization relative to other transport and fate processes, with the strong effects of agitation considered. The validity of this application has not been established.

A subsequent study by Dilling (1977) was conducted using the same experimental conditions as the 1975 study, and an average evaporative half-life of 27.2 minutes was obtained for 1 mg/l of 1,1-dichloroethene. The purpose of this subsequent study was to use the experimental data previously obtained to test two theoretical models which may be used to predict evaporative rates of slightly soluble organic compounds from water. Dilling (1977) found that the theoretical model of Mackay and Wolkoff (1973) failed to predict evaporative half-lives, but that the theoretical model of Mackay and Leinonen (1975) using the parameters of Liss and Slater (1974) correlated well with the experimental half-lives obtained. For example, the 27.7 minute evaporative half-life experimentally obtained by Dilling (1977) for 1,1-dichloroethene compared favorably to a 20.1 minute evaporative half-life predicted by the Mackay and Leinonen (1975) model but did not agree with the 0.029 minute half-life predicted by the Mackay and Wolkoff (1973) model.

Dilling (1977), however, comments that the apparent numerical agreement between his data and the values predicted by the Mackay and

Leinonen (1975) model may be fortuitous. Estimates of volatilization rates based on the Mackay and Leinonen (1975) model depend primarily on liquid-gas phase exchange rate constants, whereas the experimental model of Dilling et al. (1975) and Dilling (1977) is controlled by the rate of stirring and the wind velocity across the surface of the water.

Pearson and McConnell (1975) suggest that the presence of 1,1-dichloroethene, as well as other halogenated aliphatics, in ambient waters is due to the absorption of chloroorganics from the atmosphere by water. Aerial transport of these chloroorganics in indicated by Pearson and McConnell (1975) to play a major role in the wider distribution of these compounds and accounts for their presence in upland waters.

50.4.5 Sorption

No information pertaining specifically to the adsorption of 1,1-dichloroethene onto sediments was found. Dilling et al. (1975) carried out two closed system experiments on trichloroethene and tetrachloroethene (analogues of 1,1-dichloroethene), wherein solute loss could occur only through adsorption. Dry bentonite clay at 375 mg/l was introduced into a sealed solution and in ten minutes there was approximately a ten percent adsorption of the solute by the clay. When the amount of clay added to the closed system was doubled (750 mg/l), 22 percent of the solute was removed by adsorption in 30 minutes. The authors indicated that there appeared to be little selectivity among the various chlorinated compounds in the adsorption process. Some adsorption of trichloroethene and tetrachloroethene onto dry powdered dolomitic limestone was observed, but, again, without any selectivity among the compounds.

In the sealed system with approximately 500 mg/l peat moss, approximately 40 percent of the solutes tetrachloroethene and trichloroethene was adsorbed in 10 minutes. At longer times, no further solute removal was noted. Pearson and McConnell (1975) found no clear evidence of selective concentration of tetrachloroethene and trichloroethene in sediments; presumably, this would also be the case for 1,1-dichloroethene.

50.4.6 Bioaccumulation

According to Kopperman et al. (1976), not all organochlorine compounds bioaccumulate to high levels. The data suggest that polar compounds are more easily biodegraded, and the non-polar (highly lipophilic) compounds accumulate. Neely et al. (1974) have shown that bioaccumulation is related to the octanol/water partition coefficient (P) of the compound. The log octanol/water partition coefficient (log P) of 1.48, as calculated by the method of Hansch (Tute 1971), indicates that 1,1-dichloroethene will probably not bioaccumulate to any significant extent (see Methods section on bioaccumulation).

50.4.7 Biotransformation and Biodegradation

No information pertaining specifically to the rate of biodegradation of 1,1-dichloroethene in aquatic systems was found. According to Pearson and McConnell (1975) only completely sealed systems, such as the standard BOD (biochemical oxygen demand) bottle technique, can be used to measure biochemical degradation of volatile compounds such as 1,1-dichloroethene. The BOD bottle experiments of Pearson and McConnell have been unable to demonstrate any significant oxygen absorption from compounds containing only C, H, and Cl, thus indicating that biochemical degradation of such compounds is indeed very slow. Literature references to microbial biodegradation are few and conflicting; the majority indicate that low molecular weight chloroaliphatics are not metabolized (Pearson and McConnell 1975; McConnell et al. 1975).

50.5 Data Summary

Table 50-1 summarizes the aquatic fate discussed above. The oxidation lifetime given is a photooxidation lifetime and refers to the rate of reaction of 1,1-dichloroethene with hydroxyl radicals in the troposphere. This rate is extrapolated from the reactivity of tetrachloroethene and trichloroethene with hydroxyl radicals in the troposphere.

Due to the relatively high vapor pressure of 1,1-dichloroethene, volatilization from the aquatic system to the atmosphere is quite rapid. Once in the troposphere the compound is oxidized by hydroxyl radicals. The tropospheric lifetime of 1,1-dichloroethene is expected to be somewhat less than that of its analogues, trichloroethene and tetrachloroethene (less than 1 day and 10 days, respectively).

Table 50-1

Summary of Aquatic Fate of 1,1-Dichloroethene

Environmental Process	Summary Statement	Rate	Half-Life $(t_{1/2})$	Confidence of Data
Photolysis	Photolysis in aqueous systems is negligible; stratospheric photodissociation probably does not occur since photooxidation destroys 1,1-dichloroethene before it can reach the stratosphere.	-	-	Medium
Oxidation[a]	Photooxidation in the trosphere appears to be the predominant fate of this compound.	-	**<5-8 hours**[b]	Medium
Hydrolysis	Probably occurs too slowly to be a significant fate process.	-	~ 1 year[c]	Medium
Volatilization	Appears to be the primary transport process.	-	~ 22 to 27 minutes[d]	High
Sorption	Not much information found; probably insignificant.	-	-	Low
Bioaccumulation	Not much information found; log P in octanol/water indicates this process to be insignificant.	-	-	Low
Biotransformation/ Biodegradation	No specific information; is probably like other halogenated aliphatics in that it probably biodegrades, but at a slow rate.	-	-	Low

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a. The predominant environmental process which is thought to determine the fate of the compound.

b. This is an estimated lifetime (time for reduction to 1/e) extrapolated from the reported lifetime of trichloroethene.

c. This is an estimated maximum hydrolytic half-life extrapolated from the reported experimental half-lives of trichloroethene and tetrachloroethene.

d. Half-lives are on the order of several minutes to a few hours; depending on the degree of agitation in the system; the stated range was determined under conditions of continuous mechanical stirring at 200 rpm.

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Liss, P.S. and P.G. Slater. 1974. Flux of gases across the air-sea interface. Nature 247:181-184.

Mackay, D. and P.J. Leinonen. 1975. Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 9: 1178-1180.

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51. 1,2-trans-DICHLOROETHENE

51.1 Statement of Probable Fate

Volatilization appears to be the major transport process for removal of 1,2-trans-dichloroethene from aquatic systems. Once in the troposphere, the compound is attacked at the double bond by hydroxyl radicals, resulting in products such as formic acid, hydrochloric acid, and carbon monoxide. The tropospheric lifetime of 1,2-trans-dichloroethene based on its rate of reaction with hydroxyl radicals alone is probably much less than one day. This is an estimated lifetime extrapolated from the reported lifetime of the more highly chlorinated analogue of 1,2-trans-dichloroethene, trichloroethene. Due to the relatively high estimated reactivity of 1,2-trans-dichloroethene with hydroxyl radicals in the troposphere, it is unlikely that unreacted 1,2-trans-dichloroethene will diffuse upward to the stratosphere to undergo photodissociation.

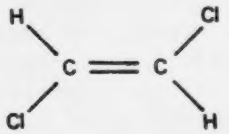
Based on the information found, it does not appear that photodissociation is a significant fate of 1,2-trans-dichloroethene in the aquatic or the atmospheric environment. This is a result of the relatively rapid volatilization from aquatic systems and the rapid rate of hydroxyl radical attack in the troposphere. Oxidation and hydrolysis in the aquatic environment do not appear to be significant for this compound, and no information was found indicating that microorganisms can readily biodegrade 1,2-trans-dichloroethene.

It has already been stated that volatilization is probably the most significant transport process of 1,2-trans-dichloroethene. There is, at present, no evidence of bioaccumulation of 1,2-trans-dichloroethene in aquatic organisms. In addition, no evidence was found pertaining to adsorption of this compound onto suspended solids or sediments.

51.2 Identification

1,2-trans-Dichloroethene has been detected in finished drinking water (Environmental Protection Agency 1975a).

The chemical structure of 1,2-trans-dichloroethene is shown below:



1,2-trans-Dichloroethene

CAS NO. 540-59-0
TSL NO. KV94000

Alternate Names

trans-1,2-Dichloroethene
trans-1,2-Dichloroethylene
trans-Acetylene dichloride
Dioform

51.3 Physical Properties

The general physical properties of 1,2-trans-dichloroethene are given below:

Molecular Weight (Weast 1977)	96.94
Melting point (Weast 1977)	-50°C
Boiling point (Weast 1977)	47.5°C
Vapor pressure at 14°C (Verschueren 1977)	200 torr
Solubility in water at 20°C (Verschueren 1977)	600 mg/l
Log octanol/water partition coefficient (Calculated by the method of Tute (1971); see Methods section on bioaccumulation)	1.48

51.4 Summary of Fate Data

51.4.1 Photolysis

No information was found pertaining specifically to the rate of photodissociation of 1,2-trans-dichloroethene in the aquatic environment. Jensen and Rosenberg (1975), however, using a closed aqueous system from which no evaporation could occur, found no significant difference in the rate of disappearance between daylight exposure and darkness for dissolved tetrachloroethene and trichloroethene, more thoroughly studied analogues of 1,2-trans-dichloroethene. From these results, it is inferred that photolysis of this compound is insignificant.

1,2-trans-Dichloroethene is quite volatile and, as a result, is rapidly transported to the troposphere. 1,2-trans-Dichloroethene is not known to undergo photodissociation in the terrestrial environment since this compound has no chromophores which absorb in the visible or near ultraviolet region of the electromagnetic spectrum (Jaffé and Orchin 1962). In addition, 1,2-trans-dichloroethene would not be expected to be available for photodissociation above the ozone layer because oxidation of 1,2-trans-dichloroethene in the troposphere is expected to occur so rapidly that no unreacted portion of the compound will survive to diffuse upward to the stratosphere.

51.3 Physical Properties

The general physical properties of 1,2-trans-dichloroethene are given below:

Molecular Weight (Weast 1977)	96.94
Melting point (Weast 1977)	-50°C
Boiling point (Weast 1977)	47.5°C
Vapor pressure at 14°C (Verschueren 1977)	200 torr
Solubility in water at 20°C (Verschueren 1977)	600 mg/1
Log octanol/water partition coefficient (Calculated by the method of Tute (1971); see Methods section on bioaccumulation)	1.48

51.4 Summary of Fate Data

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51.4.2 Oxidation

No information was found pertaining specifically to the rate of oxidation of 1,2-trans-dichloroethene in the aquatic environment. In a study of closely related analogues, trichloroethene and tetrachloroethene, Dilling et al. (1975) conducted laboratory experiments in which there was about a sixfold molar excess of dissolved oxygen compared to the total amounts of trichloroethene and tetrachloroethene. The air space above the solutions in closed systems contained approximately 90 times as much oxygen as was present in the saturated solutions. Thus, there was a large excess of oxygen present which would have been available for complete oxidation of trichloroethene and tetrachloroethene. The results obtained from samples held in the dark for 6 and 12 months indicated half-lives of 10.7 months for trichloroethene and 8.8 months for tetrachloroethane; Dilling et al. (1975) attributed the disappearance of these organochlorine compounds to oxidation.

Dilling et al. (1975) also found evidence of significant photooxidation of tetrachloroethene and trichloroethene, analogues of 1,2-trans-dichloroethene, in aqueous media in the presence of sunlight. The amounts of tetrachloroethene and trichloroethene remaining in aerated water in the dark after 12 months were approximately 13 and 20 percent greater, respectively, than the amount of tetrachloroethene and trichloroethene remaining in aerated water in the presence of sunlight. The finding that sunlight had a significant effect on the reactivity of tetrachloroethene and trichloroethene is consistent with predictions based on vapor phase photolysis studies which showed that tetrachloroethene and trichloroethene disappeared when irradiated with long wavelength light in the presence of nitric oxide or nitrogen dioxide (Altshuller and Bufalini 1971). Dilling et al. (1975) attribute the difference in disappearance of tetrachloroethene and trichloroethene in sunlight and dark to oxidation by free radicals generated by solar irradiation. It seems likely that 1,2-trans-dichloroethene would also exhibit significant photooxidation in aqueous media in the presence of sunlight since this compound is less chlorinated than tetrachloroethene and trichloroethene and, thus, may be even more amenable to attack at the double bond.

1,2-trans-Dichloroethene is quite volatile and would be expected to be transported rapidly to the troposphere. With regard to tropospheric attack of hydroxyl radicals, inferences have been drawn from the more thoroughly studied chlorinated olefins, trichloroethene and tetrachloroethene. Tetrachloroethene and trichloroethene undergo fairly rapid photooxidation in the troposphere as a result of hydroxyl radical attack at the double bond (Environmental Protection Agency 1975b). In fact, the photooxidation of tetrachloroethene and trichloroethene is so rapid that no unreacted tetrachloroethene or trichloroethene remains to diffuse to the stratosphere to undergo photodissociation by shorter wavelength, higher energy ultraviolet light (Environmental Protection Agency 1975b). According to the Environmental Protection Agency (1975b) tetrachloroethene is attacked by hydroxyl radicals more slowly than most other olefin pollutants due to the presence of four chlorine atoms. Trichloroethene, having one less chlorine atom, has been shown to be attacked more rapidly by hydroxyl radicals in the troposphere than tetrachloroethene (Gay *et al.* 1976; Environmental Protection Agency 1975b; Yung *et al.* 1975). 1,2-trans-Dichloroethene, having one less chlorine atom than trichloroethene, would be expected to be attacked even more rapidly by hydroxyl radicals.

Gay *et al.* (1976) reported photooxidation of 1,2-trans-dichloroethene to be even more rapid than photooxidation of trichloroethene and tetrachloroethene under conditions of fairly constant halocarbon to NO_2 ratios. Gay *et al.* (1976) maintain that, since this ratio is approximately constant, the reactivities of the compounds studied are at least semi-quantitative. According to Dilling *et al.* (1976), 1,2-trans-dichloroethene, cis-dichloroethene, trichloroethene, and chloroethene decomposed at moderate rates when compared with a series of standard hydrocarbons such as ethene, trans-2-butene, and others under simulated atmospheric conditions. These chlorinated compounds were reported by Dilling *et al.* (1976) to have estimated half-lives of 5 to 12 hours under bright sunlight in the presence of nitric oxide.

Pearson and McConnell (1975) exposed quartz flasks containing air to the diurnal and climatic variations of incident radiation and temperature. The air used for the experiment was not subjected to any pretreatment and was, thus, not identical in terms of its humidity or in its more detailed composition for all the experiments. Samples of air were withdrawn periodically for analysis of residual halogenated aliphatics, and approximate (50%) half-lives for organochlorines were obtained by interpolation. An interpolated tropospheric half-life of 8 weeks was obtained for 1,1-dichloroethene, an analogue of 1,2-trans-dichloroethene. This half-life, however, is probably not very accurate for two reasons. First, experiments were not set up and monitored simultaneously and, therefore, were not subject to identical conditions of solar flux and temperature. Second, the quartz flasks were not filled with the same composition of air.

Gay *et al.* (1976) reported the photooxidation products of 1,2-trans-dichloroethene to be formic acid, hydrochloric acid, and carbon monoxide. Pearson and McConnell (1975) reported the photooxidation products of an analogue of 1,2-trans-dichloroethene, 1,1-dichloroethene, irridated in air by a xenon arc and filtered to remove radiation of wavelengths below 290 nm, to be carbon monoxide, carbon dioxide, and hydrochloric acid.

51.4.3 Hydrolysis

No information was found pertaining to the rate of hydrolysis of 1,2-trans-dichloroethene. Dilling *et al.* (1975), in summarizing work by other researchers state that trichloroethene and tetrachloroethene, which are structurally similar to 1,2-trans-dichloroethene, are resistant to hydrolysis at temperatures in the range of 100°C. The presence of oxygen was reported to accelerate the decomposition of both compounds.

51.4.4 Volatilization

Dilling *et al.* (1975) reported the experimental half-life of volatilization of 1 mg/l 1,2-trans-dichloroethene from water to be 22 minutes when stirred at 200 rpm at approximately 25°C in an open container. Removal of 90 percent of the 1,2-trans-dichloroethene required 89 minutes. With stirring intermittently for 15 seconds every five minutes, the time required for 50 percent depletion of tetrachloroethene and trichloroethene, analogues of 1,2-trans-dichloroethene, was greater than 90 minutes, or on the order of four times greater than was observed during constant stirring. The presence of sodium chloride at a 3 percent concentration, as in seawater, caused about a 10 percent decrease in the chlorinated compound evaporation rate. Dilling *et al.* (1975) are careful to point out the difficulties encountered in extrapolating their laboratory results to real-world conditions, where the concentration of the organic solute would probably be very much less than 1 mg/l and where surface and bulk agitation would be highly variable. Although the data appear to be valid on a relative basis (i.e., correctly illustrating the relative rates of volatilization of chlorinated aliphatics), they cannot be used as absolute measures of volatilization rates from natural waters. For the purposes of this document, the data are used as rough-order-of-magnitude indications of the importance of volatilization relative to other transport and fate proceses, with the strong effects of agitation considered. The validity of this application has not been established.

A subsequent study by Dilling (1977) was conducted using the same experimental conditions as in the 1975 study; from the later study an average half-life of 24.0 minutes was obtained for 1 mg/l trans-1,2-dichloroethene. The purpose of this subsequent study was to use the experimental data previously obtained to test two theoretical models which may be used to predict evaporative rates of slightly soluble organic compounds from water. Dilling (1977) found that the theoretical model by Mackay and Wolkoff (1973) failed to predict evaporative half-lives while the theoretical model of Mackay and Leinonen (1975), using parameters from Liss and Slater (1974), correlated well with experimental half-lives obtained. For example, the evaporative half-life obtained experimentally for 1,2-trans-dichloroethene by Dilling (1977) was approximately 24 minutes as compared to 20.8 minutes predicted by the Mackay and Leinonen (1975) model and 0.85 minutes predicted by the Mackay and Wolkoff (1973) model. Dilling (1977), however, comments that the apparent numerical agreement between his data and the values predicted by the Mackay and Leinonen (1975) model may be fortuitous. Estimates of volatilization rates based on the Mackay and Leinonen (1975) model depend primarily on liquid-gas phase exchange rate constants, whereas the experimental model of Dilling et al. (1975) and Dilling (1977) is controlled by the rate of stirring and the wind velocity across the surface of the water.

Pearson and McConnell (1975) suggest that the presence of an analogue of 1,2-trans-dichloroethene, 1,1-dichloroethene, as well as other halogenated aliphatics, in ambient waters is due to the absorption of chloroorganics from the atmosphere by water. This process is thought to occur most effectively when the atmosphere is scrubbed as in the precipitation process. Aerial transport of these chloroorganics is indicated by Pearson and McConnell (1975) to play a major role in their wider distribution and accounts for their presence in upland waters.

51.4.5 Sorption

No information was found pertaining specifically to the adsorption of 1,2-trans-dichloroethene onto sediments. Dilling et al. (1975) carried out two closed system experiments on trichloroethene and tetrachloroethene (analogues of 1,2-trans-dichloroethene) and other chloroaliphatics, where solute loss could only be by adsorption. Dry bentonite clay at 375 mg/l was introduced into a sealed solution and after ten minutes there was approximately a ten percent adsorption by the bentonite clay compared to a blank. When the amount of clay added to the closed system was doubled (750 mg/l) there was 22 percent solute adsorption after 30 minutes. There was no further solute adsorption after this time. The authors indicated that there appeared to be little selectivity among the various chlorinated compounds in the adsorption process. The authors also observed some adsorption of trichloroethene and tetrachloroethene (and other chloroaliphatics) by dry powdered dolomitic limestone, but, again, without selectivity among the solutes.

In the sealed system with approximately 500 mg/l peat moss, approximately 40 percent of tetrachloroethene and trichloroethene was removed via adsorption in 10 minutes. At longer times, no further solute removal was noted. Pearson and McConnell (1975) found no clear evidence of selective concentration of tetrachloroethene and trichloroethene, analogues of 1,2-trans-dichloroethene, onto suspended solids or sediments.

51.4.6 Bioaccumulation

According to Kopperman et al (1976), not all organochlorine compounds bioaccumulate to high levels. The data suggest that polar compounds are more easily biodegraded, and the non-polar (highly lipophilic) compounds accumulate. Neely et al. (1974) have shown that bioaccumulation is related to the octanol/water partition coefficient (P) of the compound. The log octanol/water partition coefficient (log P) of 1.48 as calculated by the method of Hansch (Tute 1971) indicates that 1,2-trans-dichloroethene will probably not bioaccumulate to any significant extent (see Methods section on bioaccumulation).

51.4.7 Biotransformation and Biodegradation

No information was found pertaining specifically to the rate of biodegradation of 1,2-trans-dichloroethene in aquatic systems. According to Pearson and McConnell (1975) only completely sealed systems, such as the standard BOD (biochemical oxygen demand) bottle technique, can be used to measure biochemical degradation of volatile compounds such as trans-dichloroethene. The BOD bottle experiments of Pearson and McConnell have been unable to demonstrate any significant oxygen absorption from compounds containing only C, H, and Cl, thus indicating that biochemical degradation of such compounds is indeed very slow. Literature references to microbial biodegradation are few and conflicting; the majority find that low molecular weight chloroaliphatics are not metabolized (Pearson and McConnell 1975; McConnell et al. 1975).

51.5 Data Summary

Table 51-1 summarizes the aquatic fate information discussed above. The oxidation lifetime presented is a photooxidation lifetime and refers to the rate of reaction of 1,2-trans-dichloroethene with hydroxyl radicals an estimated from data on reactivity of tetrachloroethene and trichloroethene with hydroxyl radicals in the troposphere.

Due to the relatively high vapor pressure of 1,2-trans-dichloroethene, volatilization from the aquatic system to the atmosphere is quite rapid. Once in the troposphere, the compound is attacked by hydroxyl radicals at the double bond, resulting in the subsequent formation of formic acid, hydrochloric acid, carbon monoxide, and formaldehyde as reported products. The tropospheric lifetime of 1,2-trans-dichloroethene is expected to be somewhat less than that of its analogues, trichloroethene and tetrachloroethene (less than 1 day and 10 days, respectively), since 1,2-trans-dichloroethene has fewer chlorines and would be expected to be attacked more readily by hydroxyl radicals than these two analogues. Due to the relatively high extrapolated reactivity of 1,2-trans-dichloroethene with hydroxyl radicals in the troposphere, it is unlikely that unreacted 1,2-trans-dichloroethene will reach the stratosphere.

Table 51-1

Summary of Aquatic Fate of 1,2-trans-dichloroethene

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Probably does not occur since photooxidation destroys 1,2-trans-dichloroethene before it can reach the stratosphere where photodissociation would occur.	-	-	Medium
Oxidation[a]	Photooxidation in the troposphere appears to be the predominant fate of this compound.	-	< 1 day[b]	Medium
Hydrolysis	Probably occurs too slowly to be a significant fate process.	-	-	Medium
Volatilization	Appears to be the primary transport process.	-	~24 minutes[c]	Medium
Sorption	Not much information found; probably insignificant.	-	-	Low
Bioaccumulation	Not much information found; log P in octanol/water indicates this process to be insignificant.	-	-	Low
Biotransformation/ Biodegradation	No specific information, is probably like other halogenated aliphatics in that it probably biodegrades, but at a slow rate.	-	-	Low

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a. The predominant environmental process which is thought to determine the fate of the compound.

b. This is an estimated lifetime extrapolated from the reported lifetime of trichloroethene.

c. Half-lives are on the order of several minutes to a few hours, depending on the degree of agitation in the system; the value reported corresponds to a mechanically stirred condition.

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52. TRICHLOROETHENE

52.1 Statement of Probable Fate

Volatilization appears to be the primary transport process for removal of trichloroethene from aquatic systems. Once the compound enters the troposphere, hydroxyl radicals attack the double bond resulting in the subsequent formation of dichloroacetyl chloride and phosgene as the principal initial products. The tropospheric lifetime (time for reduction to 1/e of initial concentration) of trichloroethene based on its rate of reaction with hydroxyl radicals is reported to be about 4 days. Due to the relatively high reactivity of trichloroethene with hydroxyl radicals in the troposphere, it is unlikely that unreacted trichloroethene will diffuse upward to the stratosphere. The photooxidation products of trichloroethene are readily hydrolyzed.

Based on the information found, it does not appear that direct photodissociation of carbon-carbon or carbon-chlorine bonds contributes to the fate of trichloroethene in the aquatic or the atmospheric environment. This is a result of the relatively rapid volatilization from aquatic systems and the rapid rate of hydroxyl radical attack in the troposphere.

Oxidation in the aquatic environment does not appear to be a significant fate process, although there is evidence of some oxidation of trichloroethene in aqueous, closed systems in the presence of sunlight. In addition, hydrolysis, another potential fate process for compounds in the aquatic environment, probably does not occur at a sufficient rate to be important for trichloroethene. Finally, no information was found indicating that microorganisms exist which can readily degrade trichloroethene. Some information was found, however, reporting that this compound is metabolized by higher organisms leading to chlorinated acetic acid products. Chlorinated acetic acids, in turn, have been shown to be susceptible to degradation by microorganisms in seawater.

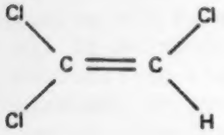
Although volatilization appears to be the most significant transport process of trichloroethene, there is some evidence of bioaccumulation of trichloroethene in marine organisms. There is, however, no evidence for biomagnification in aquatic food chains. In addition, no evidence was found of selective concentrations of trichloroethene in marine sediments, thus indicating that adsorption may not be an important transport process.

52.2 Identification

Trichloroethene is known to be ubiquitous in the environment; it has been detected in finished drinking water (Environmental Protection Agency

1975a) in drinking water supplies, in marine water, in rain water, food, human tissues (Pearson and McConnell 1975; McConnell *et al*. 1975), in the atmosphere (Pearson and McConnell 1975; McConnell *et al*. 1975; Singh *et al*. 1978), and in marine organisms (Pearson and McConnell 1975; Dickson and Riley 1976).

The chemical structure of trichloroethene is shown below.



Trichloroethene

CAS NO. 79-01-6
TSL NO. KX 45500

Alternate Name

Ethylene trichloride
Trichloroethylene
Ethinyl trichloride
(plus numerous commercial names)
Tri-Clene

52.3 Physical Properties

The general physical properties of trichloroethene are given below.

Molecular weight (Weast 1977)	131.39
Melting point (Weast 1977)	-73°C
Boiling point at 760 torr (Weast 1977)	87°C
Vapor pressure at 20°C (Pearson and McConnell 1975)	57.9 torr
Solubility in water at 20°C (Pearson and McConnell 1975)	1100 mg/l
Log octanol/water partition coefficient (Leo *et al*. 1971)	2.29

52.4 Summary of Fate Data

52.4.1 Photolysis

Little information was found pertaining specifically to the rate of direct photolysis of trichloroethene in the aqueous environment under ambient conditions. Jensen and Rosenberg (1975), using a closed system where no evaporation could occur, found no significant decrease in trichloroethene in the closed system in either daylight or darkness, thus indicating that no photolysis occurred.

Trichloroethene is quite volatile and, as a result, is rapidly transported to the troposphere. Photodissociation in the lower troposphere would not be expected to occur for trichloroethene since this compound has no chromophores which absorb in the visible or near ultraviolet region of the electromagnetic spectrum (Jaffé and Orchin 1962). Trichloroethene, however, undergoes rapid photooxidation in the troposphere; photooxidation apparently is so rapid that trichloroethene never reaches the stratosphere.

52.4.2 Oxidation

Dilling et al. (1975) found possible evidence of photooxidation of trichloroethene in aqueous media in the presence of sunlight. Dilling et al. (1975) conducted reactivity experiments in water where there was a sixfold molar excess of dissolved oxygen compared to the total amount of trichloroethene and other solutes (all chloroaliphatics). In addition, the air space above the solution in the closed system contained approximately 90 times as much oxygen as was present in the solution. Thus, there was a great excess of oxygen present which would have been available for complete oxidation of all the chlorinated compounds present.

The amount of trichloroethene remaining in aerated water stored in the dark for 12 months was approximately 20 percent greater than the amount of trichloroethene remaining in aerated water stored in the presence of sunlight. The fact that sunlight had a significant effect on the reactivity of trichloroethene is consistent with predictions based on vapor phase photolysis studies which showed that trichloroethene disappeared when irradiated with long wavelength light in the presence of nitric oxide or nitrogen dioxide (Altshuller and Bufalini 1971). Dilling et al. (1975) attribute the more rapid disappearance of trichloroethene in the presence of sunlight to free radical oxidation.

Trichloroethene is quite volatile and, as a result, is rapidly transported to the troposphere. Once the compound enters the troposphere, hydroxyl radicals attack the double bond, resulting in the subsequent formation of dichloroacetyl chloride and phosgene as the principal initial products (Environmental Protection Agency 1975c; Gay et al. 1976; Hanst

1978). These compounds are rapidly hydrolyzed at ambient conditions, resulting in HCl, CO, CO_2 and the carboxylic acid corresponding to the acid chloride (Morrison and Boyd 1973).

Yung et al. (1975) report the tropospheric lifetime (time for reduction to 1/e of initial concentration) of trichloroethene as 3.7×10^5 seconds, or about 4 days, based on its rate of reaction with hydroxyl radicals. The bimolecular rate constant for this reaction is reported to be $3 \times 10^{-12} cm^3 sec^{-1}$ (Yung et al. 1975). This rate agrees closely with the experimental data reported by Howard (1976) indicating a bimolecular rate for the reaction of approximately 2×10^{-12} cm^3 $molecule^{-1}$ sec^{-1}. The Environmental Protection Agency (1975c) has reported a half-life for trichloroethene of less than 1 day. Lillian et al. (1975) contend that the relatively low frequency of detection of trichloroethene with respect to other halogenated aliphatics is probably due to a relatively small source strength and a relatively high tropospheric reactivity. Due to the relatively high reactivity of trichloroethene with hydroxyl radicals in the troposphere, it appears unlikely that unreacted trichloroethene will reach the stratosphere.

52.4.3 Hydrolysis

In citing the works of other authors, Dilling et al. (1975) reported that trichloroethene resisted hydrolysis at 100°C. Hydrolysis of trichloroethene was reported to be accelerated by the presence of oxygen, but the products of hydrolysis from dilute solution have not been reported. Laboratory experiments by Dilling et al. (1975) were conducted in closed systems in the dark to eliminate competing processes such as volatilization and photolysis. The observed experimental half-life, which may be regarded as resulting from oxidation as well as hydrolysis, was about 10.7 months at 25°C, corresponding to a first-order rate of 0.065 $months^{-1}$ (Dilling et al. 1975). The relative contributions of oxidation and hydrolysis are not known; thus, the rate, at best, is a maximum rate for hydrolysis. According to the Environmental Protection Agency (1975b), trichloroethene is not hydrolyzed by water under normal conditions.

52.4.4 Volatilization

Dilling et al. (1975) reported the experimental half-life with respect to volatilization of 1 mg/l trichloroethene from water to be about 21 minutes (average of three) when stirred at 200 rpm at approximately 25°C in an open container. Removal of 90 percent of the trichloroethene required about 69 minutes (average of three samples). When intermittent stirring of 15 seconds duration was provided every five minutes, the time required for 50 percent depletion of trichloroethene was greater than 90 minutes. This rate is on the order of four times slower than evaporation with constant stirring. The presence of sodium chloride at a 3 percent concentration, as in seawater, caused about a 10 percent decrease in the rate of evaporation.

Evaporation appears to be the major pathway by which trichloroethene is lost from water. Dilling et al. (1975) are careful to point out the difficulties encountered in extrapolating their laboratory results to real-world conditions, where the concentration of the organic solute would probably be very much less than 1 mg/l and where surface and bulk agitation would be highly variable. Although the data appear to be valid on a relative basis (i.e., correctly illustrating the relative rates of volatilization of chlorinated aliphatics), they cannot be used as absolute measures of volatilization rates from natural waters. For the purposes of this document, the data are used as rough-order-of-magnitude indications of the importance of volatilization relative to other transport and fate proceses, with the strong effects of agitation considered. The validity of this application has not been established.

A subsequent study by Dilling (1977) was conducted using the same experimental conditions as in the 1975 study, and an evaporative half-life range for trichloroethene of 17.7 to 23.5 minutes was obtained for 0.94 to 0.96 mg/l. The purpose of this subsequent study was to use the experimental data obtained to test two theoretical models formulated to predict rates of evaporation of slightly soluble organic compounds from water. Dilling (1977) found that the theoretical model by Mackay and Wolkoff (1973) failed to predict evaporative half-lives, but that evaporative half-lives predicted by the model of Mackay and Leinonen (1975), using parameters of Liss and Slater (1974), correlated well with experimental data. For example, the evaporative half-life of 23.8 minutes for trichloroethene predicted by the Mackay and Leinonen model is very close to the range of 17.7 to 23.5 minutes determined by Dilling (1977), in contrast to the much lower half-life of 0.47 minutes predicted by the Mackay and Wolkoff (1973) model.

Dilling (1977), however, comments that the apparent numerical agreement between his data and the values predicted by the Mackay and Leinonen (1975) model may be fortuitous. Estimates of volatilization rates based on the Mackay and Leinonen (1975) model depend primarily on liquid-gas phase exchange rate constants, whereas the experimental model of Dilling et al. (1975) and Dilling (1977) is controlled by the rate of stirring and the wind velocity across the surface of the water.

In a study by Pearson and McConnell (1975), rainwater collected in Runcorn, England contained up to 1.5 x 10^{-10} parts (by mass) of trichloroethene. Municipal waters supplied to the cities of Liverpool, Chester, and Manchester (all supplied from upland surface sources) contained up to 6 x 10^{-9} parts (by mass) trichloroethene. While entry to the environment appears to be predominantly evaporative, there may also be some chloro-organics in aqueous industrial effluents which will pass into municipal drainage systems and rivers. Mackay and Wolkoff (1973) have shown that the evaporation rate of poorly soluble species from water can be quite high due to their high activity coefficients. Pearson and McConnell (1975) and McConnell et al. (1975) point out that this is a reversible process since water will absorb chloroorganics from the atmosphere, a process which will occur most effectively when the atmosphere is scrubbed during periods of rainfall. The presence of trace organochlorines, including trichloroethene, in upland waters is believed to be due to aerial transport (Pearson and McConnell 1975; McConnell et al. 1975).

A study by Jensen and Rosenberg (1975) indicates that the rate of volatilization of trichloroethene proceeds more rapidly than photolysis, oxidation, or hydrolysis. An initial concentration between 0.1 to 1 mg/l trichloroethene in a 20 liter volume of water was found to decrease 80 percent after 8 days in an aquarium kept in light and partly open. Tetrachloroethene initially present at the same concentrations in a closed system exposed to daylight and a closed system exposed to dark showed less than about a 5 percent disappearance in 8 days.

Assuming that all processes involved are first order, the data of Jensen and Rosenberg (1975) indicate the evaporative half-life for trichloroethene in the partly open (and supposedly quiescent) aquarium to be 3.44 days, which is apparently comparable to the data of Dilling et al. (1975), indicating a 21 minute half-life under continuous stirring at 200 rpm and over 90 minutes under discontinuous stirring (15 seconds per five minutes). These results illustrate the marked effect of system agitation on volatilization rate from water for compounds such as trichloroethene.

52.4.5 Sorption

Dilling et al. (1975) carried out two closed system experiments where solute loss could only be by adsorption. Dry bentonite clay at 375 mg/l was introduced into a sealed solution, and, in ten minutes, there was approximately a ten percent adsorption of trichloroethene, as well as four other chlorinated compounds, by the clay compared to a blank. When the amount of clay added to the closed system was doubled (750 mg/l) there was 22 percent solute adsorption after 30 minutes. There was no further solute adsorption after this time. The authors indicated that there appeared to be little selectivity among the various chlorinated compounds in the adsorption process. The authors observed some adsorption of trichloroethene by dry powdered dolomitic limestone, but, again, without selectivity among the solutes used.

In the sealed system with approximately 500 mg/l peat moss, approximately 40 percent of the trichloroethene was adsorbed in 10 minutes. At longer times, no further solute removal was noted. The subsequent decrease in the rate of disappearance of trichloroethene at longer time periods than 10 minutes was suggested to be due to gradual release or desorption of trichloroethene from the peat moss to the solution.

Pearson and McConnell (1975) found that the concentration of trichloroethene in Liverpool Bay (England) sediments varied from a few parts per 10^{12} (by mass) to a maximum of 9.9×10^{-9}. Samples of marine sediment from Liverpool Bay contained the same compounds as the overlying waters, but there was no correlation between the chloroorganic content of the sediment and that of the mid-depth water from the same point on the sampling grid (Pearson and McConnell 1975; McConnell et al. 1975). In addition, Pearson and McConnell (1975) reported that there was no apparent relation between high concentrations and geographical features, as was noticed in the case of the water samples, nor was there any correlation between concentration in the sediment and particle size. In general, there was no clear evidence of selective concentration of trichloroethene in sediments. McConnell et al. (1975), however, did note that coarse gravels have little adsorptive capacity for trichloroethene, whereas sediments rich in organic detritus have a much higher adsorptive capacity. They also noted that, averaged over all samples, the concentrations of chlorinated C_1/C_2 compounds (including trichloroethene) in the sediments were similar to those in the water.

52.4.6 Bioaccumulation

According to Kopperman et al. (1976) not all organochlorine compounds bioaccumulate to high levels. The data suggest that polar compounds are more easily biodegraded, and the non-polar (highly lipophilic) compounds accumulate. In addition, Kopperman et al. (1976) point out that the incorporation of chlorine compounds during the disinfection of waste effluents with chlorine is an undesirable end result of effluent treatment in that chlorinated compounds become more persistent and bioaccumulate to a greater extent. In this study it was found that the concentration of trichloroethene in water from sewage treatment plants was 40.2 μg/l in influent before treatment. The effluent before chlorination contained 8.6 μg/l, whereas the effluent after chlorination contained 9.8 μg/l trichloroethene. Neely et al. (1974) have shown that bioaccumulation is directly related to the octanol/water partition coefficient (P) of the compound. The log octanol/water partition coefficient (log P) of 2.29 for trichloroethene as determined by Leo et al. (1971) indicates that bioaccumulation is possible for this compound, but the process is probably not important in comparison to volatilization as a removal mechanism.

Pearson and McConnell (1975) determined the level of trichloroethene and other chlorinated hydrocarbons in the tissues of a wide range of organisms. Species were chosen to represent significant trophic levels in the marine environment. Due to the occurrence of high levels of PCB and DDT in fish-eating birds, special attention has been paid to marine and brackish water birds. The maximum overall increase in concentration between seawater and the tissues of animals at the top of food chains (such as fish liver, sea bird eggs, and sea seal blubber) was less than 100-fold for trichloroethene (from 0.5×10^{-9} in water to 50×10^{-9} in tissues).

Although evidence for weak to moderate bioaccumulation of trichloroethene by marine organisms exists (Pearson and McConnell 1975), there is no evidence for biomagnification of trichloroethene in aquatic food chains.

McConnell et al. (1975) report that there is evidence of the presence of trichloroethene in human tissue at extremely low concentrations. It is indicated, however, that there is no evidence for significant accumulation in human tissue. According to McConnell et al. (1975), these data indicate a general background, at the µg/l level, which pervades the atmosphere, hydrosphere, and biosphere.

52.4.7 Biotransformation and Biodegradation

No information was found pertaining specifically to the rate of biodegradation of trichloroethene in aquatic systems. Thom and Agg (1975) have included trichloroethene in a list of synthetic organic chemicals which should be degradable by biological sewage treatment provided suitable acclimatization can be achieved. They note, however, that not many compounds in this list occur free in nature and, as a result, it is unlikely that microorganisms already possess the ability to destroy them. The authors consider trichloroethene, along with various other compounds, to be potentially biodegradable.

According to Pearson and McConnell (1975) only completely sealed systems, such as the standard BOD (biochemical oxygen demand) bottle technique, can be used to measure biochemical degradation of volatile compounds such as trichloroethene. The BOD bottle experiments of Pearson and McConnell have been unable to demonstrate any significant oxygen absorption from compounds containing only C, H, and Cl, thus indicating that biochemical degradation of such compounds is indeed very slow.

There is some evidence from mammal studies that trichloroethene can be metabolized by higher organisms (Pearson and McConnell 1975; McConnell et al. 1975). Metabolism of trichloroethene results in the formation of dichloroacetic acid (Pearson and McConnell 1975).

Literature references to microbial biodegradation of compounds such as trichloroethene are few and conflicting; the majority report that low molecular weight chloroaliphatics are not metabolized (Pearson and McConnell 1975; McConnell et al. 1975). In mammals, the metabolic pathways of trichloroethene lead to chlorinated acetic acids, either directly or via chloroethanols. Chlorinated acetic acids have all been shown to be susceptible to further degradation by microorganisms in seawater (Pearson and McConnell 1975). McConnell *et al*. (1975) conclude that the simple chloroaliphatic compounds are not particularly persistent, and that their degradation products are simple species commonly found in the environment.

52.5 Data Summary

Table 52-1 summarizes the aquatic fate information discussed above. The oxidation rate presented is a photooxidation rate and refers to the rate of reaction of trichloroethene with hydroxyl radicals in the troposphere.

Due to the relatively high vapor pressure of trichloroethene, volatilization from the aquatic system to the atmosphere is quite rapid. Once in the troposphere, hydroxyl radicals attack the double bond, resulting in the subsequent formation of dichloroacetyl chloride and phosgene as the principal products. The tropospheric lifetime of trichloroethene based on its rate of reaction with hydroxyl radicals is reported to be 3.7×10^5 seconds, corresponding to a lifetime of about 4 days. Due to the relatively high reactivity of trichloroethene with hydroxyl radicals in the troposphere, it is unlikely that unreacted trichloroethene will reach the stratosphere.

Table 52-1

Summary of Aquatic Fate of Trichloroethene

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Probably does not occur since photooxidation destroys trichloroethene before it can reach the stratosphere, which is the region above the ozone layer where direct photolysis could occur.	-	-	High
Oxidation[a]	Photooxidation in the troposphere appears to be the predominant fate of this compound; photooxidation in the aquatic environment occurs at a slow rate; direct oxidation at ambient conditions does not occur in the aquatic or atmospheric environment.	$3\times10^{-12}cm^3sec^{-1}$	~4 days[b]	High
Hydrolysis	Probably occurs too slowly to be a significant fate process.	0.065 $months^{-1}$[c]	10.7 months	High
Volatilization	The primary transport process.	-	~20 minutes[d]	High
Sorption	Probably not important.	-	-	Medium
Bioaccumulation	There is evidence of some bioaccumulation by marine organisms, but there is no evidence of biomagnification up the food chain.	-	-	Medium
Biotransformation/ Biodegradation	There is evidence that metabolic products of trichloroethene from higher organisms can be biodegraded by microorganisms in sea water.	-	-	Medium

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a. The predominant environmental process which is thought to determine the fate of the compound.

b. Reported as a lifetime of ~3.7×10^5 seconds, corresponding to a lifetime of about 4 days.

c. Hydrolysis rate is probably a maximum rate.

d. Half-lives are on the order of several minutes to a few days, depending on the degree of agitation; the value presented was determined under conditions of continuous mechanical stirring at 200 rpm.

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53. TETRACHLOROETHENE (PERCHLOROETHYLENE)

53.1 Statement of Probable Fate

Volatilization appears to be the major transport process for removal of tetrachloroethene from aquatic systems. Once in the troposphere, the compound reportedly reacts with hydroxyl radicals which attack the double bond, resulting in the formation of trichloroacetylchloride as the principal product, with phosgene being produced to a lesser extent. The tropospheric lifetime of tetrachloroethene based on its rate of reaction with hydroxyl radicals is reported to be about 10 days. On this basis, it is unlikely that unreacted tetrachloroethene will diffuse upward to the stratosphere.

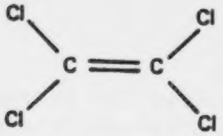
Based on the information found it does not appear that photodissociation is a significant fate of tetrachloroethene in the aquatic or the atmospheric environment. Oxidation in the aquatic environment does not appear to be significant, although there is evidence of some oxidation of tetrachloroethene in aqueous, closed systems in the presence of sunlight. In addition, hydrolysis, another potential fate process for compounds in the aquatic environment, probably does not occur at a significant rate to be important for tetrachloroethene. Finally, no information was found indicating that microorganisms exist which can readily biodegrade tetrachloroethene. Some information, however, was found reporting this compound to be metabolized by higher organisms leading to chlorinated acetic acid products. Chlorinated acetic acids, in turn, have been shown to be susceptible to degradation by microorganisms in seawater.

Although volatilization appears to be the most significant transport process, there is some evidence of bioaccumulation of tetrachloroethene in marine organisms. There is, however, no evidence for biomagnification in aquatic food chains. In addition, no evidence was found of selective concentration of tetrachloroethene in marine sediments, thus indicating that adsorption is probably not an important transport process for this compound.

53.2 Identification

This compound is known to be ubiquitous in the environment. Tetrachloroethene has been detected in finished drinking water (Environmental Protection Agency 1975a), in marine and rain water, in food, in human tissues, in the atmosphere (Pearson and McConnell 1975; McConnell *et al*. 1975; Singh *et al*. 1978), and in marine organisms (Dickson and Riley 1976).

The chemical structure of tetrachloroethene is shown below:



Tetrachloroethene

CAS NO. 127-18-4
TSL NO. KX 38500

Alternate Names
Perchloroethylene
Ethylene tetrachloride
Tetrachloroethylene
Perchloroethene

53.3 Physical Properties

The general physical properties of tetrachloroethene are given below.

Molecular weight (Weast 1977)	165.83
Melting point (Verschueren 1977)	-22.7°C
Boiling point at 760 torr (Weast 1977)	121°C
Vapor pressure at 20°C (Pearson and McConnell 1975)	14 torr
Solubility in water at 20°C	150 to 200 mg/1*
Log octanol/water partition coefficient (Neely _et al_. 1974)	2.88

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*Several values for solubility of tetrachloroethene in water at 20°C were found in the literature. These values range from 150 mg/l (Pearson and McConnell 1975) to 200 mg/l (Chiou _et al_. 1977).

53.4 Summary of Fate Data

53.4.1 Photolysis

Relatively little information was found pertaining specifically to the rate of photodissociation of tetrachloroethene in the aqueous environment under ambient conditions. Jensen and Rosenberg (1975), using a closed system where no evaporation could occur, found no significant difference in loss of tetrachloroethene between daylight exposure and darkness, thus indicating that no photolysis occurred. These tests utilized both seawater and deionized and boiled fresh water.

Tetrachloroethene is quite volatile and, as a result, is rapidly transported to the troposphere. Tetrachloroethene is attacked by hydroxyl radicals more slowly than most other olefin pollutants due to the presence of four chlorine atoms (Environmental Protection Agency 1975c). According to the Environmental Protection Agency (1975c), there is only a remote possibility that reaction of tetrachloroethene with hydroxyl radicals is sufficiently slow to allow a portion of the tetrachloroethene in the troposphere to diffuse upward to the stratosphere. Photodissociation in the terrestrial environment would not be expected to occur for tetrachloroethene since this compound has no chromophores which absorb in the visible or near ultraviolet region of the electromagnetic spectrum (Jaffé and Orchin 1962).

53.4.2 Oxidation

The literature reviewed indicates that oxidation probably does not play a significant role in the aquatic fate of tetrachloroethene. Dilling et al. (1975) conducted laboratory experiments in which there was about a sixfold molar excess of dissolved oxygen compared to the total amount of tetrachloroethene. In addition, the air space above the solution in the closed system contained approximately 90 times as much oxygen as was present in the saturated solution. Thus, there was a great excess of oxygen present which would have been available for complete oxidation of all the chlorinated compounds present. Their results indicated that volatilization was much more rapid than any oxidative process which may have occurred.

Dilling et al. (1975) did find evidence of significant photooxidation of tetrachloroethene in aqueous media in the presence of sunlight. The amount of tetrachloroethene remaining in aerated water in the dark after 12 months was approximately 13 percent greater than the amount of tetrachloroethene remaining in aerated water in the presence of sunlight. The fact that sunlight had a significant effect on the reactivity of tetrachloroethene is consistent with predictions based on vapor phase photolysis studies which showed that tetrachloroethene disappeared when irridiated with long wavelength light in the presence of nitric oxide or nitrogen dioxide (Altshuller and Bufalini 1971). Dilling et al. (1975) attribute the difference in disappearance of tetrachloroethene between samples exposed to sunlight and those held in the dark to oxidation by free radicals.

Tetrachloroethene is quite volatile and, as a result, is rapidly transported to the troposphere. Once in the troposphere, hydroxyl radicals attack the double bond, resulting in the subsequent formation of trichloroacetylchloride as the principal initial product, with phosgene being produced to a lesser extent (Andersson _et al_. 1975; Hanst 1978; Environmental Protection Agency 1975c; Gay _et al_. 1976). Both of these compounds are readily hydrolyzed at ambient conditions (Morrison and Boyd 1973). Tetrachloroethene, however, is attacked by hydroxyl radicals more slowly than most other olefin pollutants due to the presence of four chlorine atoms (Environmental Protection Agency 1975c). According to Yung _et al_. (1975) the tropospheric lifetime of tetrachloroethene based on its rate of reaction with hydroxyl radicals is reported to be 8.5×10^5 seconds, corresponding to a lifetime of about ten days. The bimolecular rate constant for this reaction is reported to be $1.3 \times 10^{-12} cm^3 sec^{-1}$ (Yung _et al_. 1975). The experimental data of Howard (1976) indicate a bimolecular rate of about 1.7×10^{-13} cm^3 $molecule^{-1}$ sec^{-1}. Lillian _et al_. (1975) contend that the low concentrations of tetrachloroethene found in the atmosphere serve as evidence for high tropospheric reactivity.

53.4.4 Hydrolysis

In citing the works of other authors, Dilling _et al_. (1975) reported that tetrachloroethene was unreactive hydrolytically at 150°C in the absence of oxygen. The decomposition of tetrachloroethene, however, was reported to be accelerated by the presence of oxygen. Trichloroacetic and hydrochloric acids have been reported as products. Laboratory experiments by Dilling _et al_. (1975) were conducted in closed systems in the dark to eliminate competing processes such as volatilization and photolysis. The experimental hydrolytic half-life obtained was about 8.8 months at 25°C, corresponding to a first-order rate of 0.079 $months^{-1}$ which should be considered a maximum rate for hydrolysis.

According to the Environmental Protection Agency (1975b) pure tetrachloroethene in contact with water for long periods of time decomposes to trichloroacetic acid and hydrogen chloride.

53.4.4 Volatilization

Dilling _et al_. (1975) reported the experimental volatilization half-life of 1 mg/l tetrachloroethene in water to be 26 minutes (average of three samples) when stirred at 200 rpm at approximately 25°C in an open container. Removal of 90 percent of the tetrachloroethene required 83 minutes (average of three samples). With intermittent stirring for 15 seconds every five minutes the time required for 50 percent depletion of tetrachloroethene was greater than 90 minutes, which is on the order of three times greater than that observed during constant stirring. The presence of sodium chloride at a 3 percent concentration, as in seawater, caused about a 10 percent decrease in the chlorinated compound evaporation rate.

Evaporation appears to be the major pathway by which tetrachloroethene is lost from water. Dilling et al. (1975) are careful to point out the difficulties encountered in extrapolating their laboratory results to real-world conditions, where the concentration of the organic solute would probably be very much less than 1 mg/l and where surface and bulk agitation would be highly variable. Although the data appear to be valid on a relative basis (i.e., correctly illustrating the relative rates of volatilization of chlorinated aliphatics), they cannot be used as absolute measures of volatilization rates from natural waters. For the purposes of this document, the data are used as rough-order-of-magnitude indications of the importance of volatilization relative to other transport and fate proceses, with the strong effects of agitation considered. The validity of this application has not been established.

A subsequent study by Dilling (1977) was conducted using the same experimental conditions as in the 1975 study, and an average half-life range of 20.2 to 27.1 minutes was obtained for 0.92 mg/l tetrachloroethene. The purpose of this subsequent study was to use the experimental data obtained to test two theoretical models formulated to predict evaporative rates of slightly soluble organic compounds from water. Dilling (1977) found that the theoretical model of Mackay and Wolkoff (1973) failed to predict evaporative half-lives but that the model of Mackay and Leinonen (1975) using the parameters of Liss and Slater (1974) correlated well with the experimental half-lives obtained by Dilling (1977). For example, the evaporative half-life obtained experimentally by Dilling (1977) was approximately 20 to 27 minutes, compared to 26.5 minutes predicted by the Mackay and Leinonen (1975) model and 0.20 minutes predicted by the Mackay and Wolkoff (1973) model. Dilling (1977), however, comments that the apparent numerical agreement between his data and the values predicted by the Mackay and Leinonen (1975) model may be fortuitous. Estimates of volatilization rates based on the Mackay and Leinonen (1975) model depend primarily on liquid-gas phase exchange rate constants, whereas the experimental model of Dilling et al. (1975) and Dilling (1977) is controlled by the rate of stirring and the wind velocity across the surface of the water.

In a study by Pearson and McConnell (1975), rainwater collected in Runcorn, England contained up to 1.5 x 10^{-10} (by mass) of tetrachloroethene. Municipal waters supplied to the cities of Liverpool, Chester, and Manchester (all supplied from upland surface sources) contained up to 3.8 x 10^{-10} (by mass) tetrachloroethene. While entry to the general environment appears to be predominantly evaporative, there may also be some chloroorganics in aqueous industrial effluents which will pass into municipal drainage systems and rivers. Mackay and Wolkoff (1973) have shown that the evaporation rate of poorly soluble species from water can be quite high due to their high activity coefficients. Pearson and McConnell (1975) and McConnell et al. (1975) point out that this is a reversible process since water will absorb chloroorganics from the atmosphere, a process which will occur most effectively when the atmosphere is scrubbed during periods of rainfall. The presence of trace organochlorines, including tetrachloroethene, in upland waters is believed to be due to aerial transport (Pearson and McConnell 1975; McConnell et al. 1975).

A study by Jensen and Rosenberg (1975) indicates that the rate of volatilization of tetrachloroethene proceeds more rapidly than photolysis, oxidation, or hydrolysis. An initial concentration between 0.1 to 1 mg/l tetrachloroethene in 20 liters of water was found to decrease 50 percent after 8 days in a partially open, well lit aquarium. Tetrachloroethene initially present at the same concentration in closed systems either exposed to daylight or held in the dark was reduced only 5 percent after 8 days demonstrating that volatilization was more rapid than photolysis.

53.4.5 Sorption

Dilling et al. (1975) carried out two closed system experiments where solute loss could be only by adsorption. Dry bentonite clay at 375 mg/l was introduced into a sample, and in ten minutes there was approximately a ten percent adsorption of tetrachloroethene, as well as other chlorinated compounds, by the clay (compared to a blank). When the amount of clay added to the closed system was doubled (750 mg/l) there was 22 percent solute loss via adsorption after 30 minutes. There was no further solute adsorption after this time. The authors indicated that there appeared to be little selectivity among the various chlorinated compounds in the adsorption process.

The authors observed some adsorption of tetrachloroethene by dry powdered dolomitic limestone, but, again, without any significant selectivity among haloaliphatic species.

In the sealed system to which had been added approximately 500 mg/l peat moss, approximately 40 percent of the tetrachloroethene was lost via adsorption within 10 minutes. At longer times, no further solute removal was noted.

Pearson and McConnell (1975) found that the concentrations of tetrachloroethene in Liverpool Bay sediments varied from a few parts per 10^{12} (by mass) to a maximum of 4.8×10^{-9}. Samples of marine sediment from Liverpool Bay contained the same compounds as the overlying waters, but there was no correlation between the chloroorganic content of the sediment and that of the mid-depth water from the same point on the sampling grid (Pearson and McConnell 1975; McConnell *et al*. 1975). In addition, Pearson and McConnell (1975) reported that there was no apparent relation between high concentrations and geographical features, as was noticed in the case of the water samples, nor was there any correlation between concentration in the sediment and particle size. In general, there was no clear evidence of selective concentration of tetrachloroethene in sediments. McConnell *et al*. (1975), however, did note that coarse gravels have little adsorptive capacity for tetrachloroethene, whereas sediments rich in organic detritus have a much higher adsorptive capacity. They also note that, averaged over all samples, the concentrations of chlorinated C_1/C_2 compounds (including tetrachloroethene) in the sediments were similar to those in the water.

53.4.6 Bioaccumulation

According to Kopperman *et al*. (1976) not all organochlorine compounds bioaccumulate to high levels. The data suggest that polar compounds are more easily biodegraded, and the non-polar (highly lipophilic) compounds accumulate. In addition, Kopperman *et al*. (1976) point out that the formation of chlorine compounds during the disinfection of waste effluents with chlorine is an undesirable end result of effluent treatment in that chlorinated compounds become more persistent and bioaccumulate to a greater extent. In this study it was found that the concentration of tetrachloroethene in water from sewage treatment plants was 6.2 μg/l in influent before treatment. The effluent before chlorination contained 3.9 μg/l tetrachloroethene, whereas the effluent after chlorination contained 4.2 μg/l tetrachloroethene.

Neely *et al*. (1974) have shown that bioaccumulation is directly related to the octanol/water partition coefficient (P) of the compound. The log octanol/water partition coefficient (log P) of 2.88 for tetrachloroethene as determined by Neely *et al*. (1974) indicates that this compound may have the potential to bioaccumulate.

Pearson and McConnell (1975) determined the level of tetrachloroethene and other chlorinated hydrocarbons in the tissues of a wide range of organisms. Species were chosen to represent significant trophic levels in the marine environment. Due to the occurrence of high levels of PCB and DDT in fish-eating birds, special attention was paid to marine and brackish water birds. The maximum overall increase in concentration between seawater and the tissues of animals at the top of food chains (such as fish liver, sea bird eggs, and seal blubber) was on the order of 100-fold for tetrachloroethene (from 0.5×10^{-9} in water to 50×10^{-9} in tissue).

Pearson and McConnell (1975) conducted laboratory experiments to assess bioaccumulation of tetrachloroethene and other chloroorganics via direct diffusion across wetted membranes. The first experiments by Pearson and McConnell (1975) have indicated that bioaccumulation occurs, but that this bioaccumulation is not accompanied by any detected ill effects. From experiments in which dabs were exposed to tetrachloroethene it was found that the accumulation factor is less than 10 in the flesh, and more than 100 in the liver. In general, it was found that concentrations in fatty tissues such as liver are much higher than those in muscle and that the ratios of concentration in different organs are proportional to fat content.

Although evidence for weak to moderate bioaccumulation of tetrachloroethene by marine organisms exists as discussed above, there is no evidence for biomagnification of tetrachloroethene in aquatic food chains.

McConnell *et al*. (1975) report that there is evidence of the presence of tetrachloroethene in human tissue at extremely low concentrations. It is indicated, however, that there is no evidence for significant accumulation in human tissue. According to McConnell *et al*. (1975), these data indicate a general background, at the μg/l level, which pervades the atmosphere, hydrosphere, and biosphere.

53.4.7 Biotransformation and Biodegradation

No information was found pertaining specifically to the rate of biodegradation of tetrachloroethene in aquatic systems. Thom and Agg (1975) have included tetrachloroethene in a list of synthetic organic chemicals which should be degradable by biological sewage treatment provided suitable acclimatization can be achieved. They note, however, that not many compounds in this list occur free in nature and, as a result, it is unlikely that microorganisms already possess the ability to destroy them. Thom and Agg (1975) consider tetrachloroethene to be potentially biodegradable.

According to Pearson and McConnell (1975) only completely sealed systems, such as the standard BOD (biochemical oxygen demand) bottle technique, can be used to measure biochemical degradation of volatile compounds such as tetrachloroethene. The BOD bottle experiments of Pearson and McConnell have been unable to demonstrate any significant oxygen absorption from compounds containing only C, H, and Cl, thus indicating that biochemical degradation of such compounds is indeed very slow.

There is some evidence from mammal studies that tetrachloroethene can be metabolized by higher organisms (Pearson and McConnell 1975; McConnell *et al*. 1975). Metabolism of tetrachloroethene results in the formation of trichloroacetic acid.

Literature references to microbial biodegradation of compounds similar to tetrachloroethene are few and conflicting; the majority find that low molecular weight chloroaliphatics are not metabolized (Pearson and McConnell 1975; McConnell et al. 1975).

In mammals, the metabolic pathways of tetrachloroethene lead to chlorinated acetic acids, either directly or via chloroethanols. Chlorinated acetic acids have all been shown to be susceptible to further degradation by microorganisms in seawater (Pearson and McConnell 1975). McConnell et al. (1975) concluded that the simple chloroaliphatic compounds are not particularly persistent, but that their degradation products are simple chemical species commonly found in the environment.

53.5 Data Summary

Table 53-1 summarizes the aquatic fate discussed above. The oxidation rates presented are a photooxidation rates and refer to the rate of reaction of tetrachlorethene with hydroxyl radicals in the troposphere.

Due to the relatively high vapor pressure of tetrachloroethene, volatilization from the aquatic system to the atmosphere is quite rapid. Once in the troposphere, the compound reacts with hydroxyl radicals at the double bond, resulting in the subsequent formation of trichloroacetyl chloride as the principal product with phosgene being produced to a lesser extent. The tropospheric lifetime of tetrachloroethene based on its rate of reaction with hydroxyl radicals is reported to be 8.5×10^5 seconds, corresponding to a lifetime of about 10 days. Due to the relatively high reactivity of tetrachloroethene with hydroxyl radicals in the troposphere, it appears unlikely that unreacted tetrachloroethene will reach the stratosphere.

Table 53-1

Summary of Aquatic Fate of Tetrachloroethene

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Probably does not occur. Photooxidation destroys tetrachloroethene before it can reach the stratosphere, which is the region above the ozone layer where direct photolysis could occur.	-	-	High
Oxidation[a]	Photooxidation in the troposphere appears to be the predominant fate of this compound; photooxidation in the aquatic environment occurs at a slow rate; direct oxidation at ambient conditions does not occur in the aquatic or atmospheric environment.	$1.3\times10^{-12}\ cm^3\ sec^{-1}$ $1.7\times10^{-13}\ cm^3 molecule^{-1} sec^{-1}$	~10 days[b]	High
Hydrolysis	Probably occurs too slowly to be a significant fate process.	0.079 $months^{-1}$[c]	8.8 months	Medium
Volatilization	The primary transport process.	-	~20-30 minutes[d]	High
Sorption	Probably not important.	-	-	Medium
Bioaccumulation	There is evidence of bioaccumulation by marine organisms, but there is no evidence of biomagnification up the food chain.	-	-	Medium
Biotransformation/ Biodegradation	There is evidence that metabolic products of tetrachloroethene from higher organisms can be biodegraded by microorganisms in sea water.	-	-	Medium

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a. The predominant environmental process which is thought to determine the fate of the compound.

b. Reported as a lifetime of ~8.5×10^5 seconds, corresponding to a lifetime of about 10 days.

c. Hydrolysis rate is probably a maximum rate.

d. Half-lives are on the order of several minutes to a few hours, depending on the degree of agitation. This half-life is based on a stirring rate of 200 rpm in the experimental systems of Dilling (1977) and Dilling et al. (1975).

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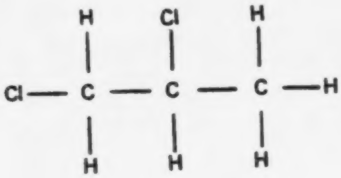
54. 1,2-DICHLOROPROPANE

54.1 Statement of Probable Fate

1,2-Dichloropropane exhibits the general chemical stability typical of the short-chain chloroaliphatics. The most rapid process by which this chemical is transported from the aquatic environment appears to be volatilization. Although the molecules may be destroyed in the troposphere through reaction with hydroxyl radicals, it is expected that a portion will be reintroduced to the surface waters through precipitation. The aquatic fate of this compound is probably hydrolysis.

54.2 Identification

1,2-Dichloropropane has been detected in finished drinking water, surface water, and industrial effluents (Shackelford and Keith 1976). The chemical structure of 1,2-dichloropropane is shown below.



$Cl-CH_2-CHCl-CH_3$

1,2-Dichloropropane

CAS NO. 78-87-5
TSL NO. TX 96250

Alternate Names

Propylene chloride
Propylene dichloride

54.3 Physical Properties

The general physical properties of 1,2-dichloropropane are as follows.

Molecular weight (Verschueren 1977)	112.99
Melting point (Verschueren 1977)	-100°C
Boiling point at 760 torr (Verschueren 1977)	96.8°C
Vapor pressure at 20°C (Verschueren 1977)	42 torr

Solubility in water at 20°C (Verschueren 1977)	2,700 mg/l
Log octanol/water partition coefficient (Calculated as per Tute 1971)	2.28

54.4 Summary of Fate Data

54.4.1 Photolysis

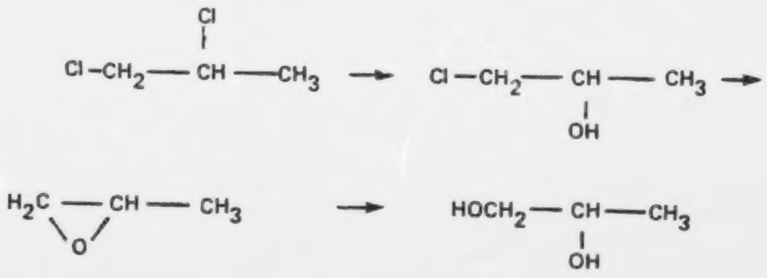
1,2-Dichloropropane does not have any chromophores that will absorb electromagnetic radiation in the ultraviolet or visible spectral regions (Jaffé and Orchin 1962). Direct photolysis is thus not expected to be an important aquatic fate process, although no specific experimental data were found to support this view.

54.4.2 Oxidation

No data were found concerning the oxidation of 1,2-dichloropropane. Based upon the results of Dilling et al. (1975) with short-chain (one and two carbon) chloroaliphatics, oxidation does not appear to be important as an aquatic fate for this type of compound. This does not preclude the possibility of oxidation in the atmosphere after volatilization; tropospheric photooxidation by hydroxyl radicals is probably important

54.4.3 Hydrolysis

No environmentally relevant kinetic data were found for the hydrolysis of this compound. Dilling et al. (1975) showed that the half-lives with respect to hydrolysis for one and two carbon chloroaliphatics are six months to several years. 1,2-Dichloropropane should be expected to have a similar uncatalyzed rate of hydrolysis. If this compound is adsorbed by clay, base catalyzed hydrolysis could ultimately lead to 1,2-propanediol. This reaction sequence shown below is based upon standard preparative procedures. Clay surfaces are known to facilitate both acid and base catalyzed reactions in an aqueous environment (Gabel and Ponnamperuma 1967).



54.4.4 Volatilization

According to Dilling *et al.* (1975), the half-lives with respect to volatilization from water for 1,2,3-trichloropropane and 1,2,2,3-tetrachloropropane are 51 minutes and 47 minutes, respectively. The initial concentration of each was 1 mg/l in an open, stirred container. Analogously, 1,2-dichloropropane, which is more volatile than either of the more highly halogenated chloroaliphatics mentioned above, should be expected to have a half-life equal to or less than 50 minutes under the conditions used by Dilling *et al*. (1975). Once volatilized, this compound will be returned to the soil and surface water via precipitation unless oxidized in the atmosphere. Dilling *et al*. (1975) have pointed out the difficulty in extrapolating their laboratory data to environmental conditions, but volatilization half-lives can be expected to be on the order of one to several hours, depending on conditions.

54.4.5 Sorption

No data were found concerning adsorption of 1,2-dichloropropane onto particulates and sediments. A log P (log octanol/water partition coefficient) of 2.28 can be calculated for this compound based on the method of Tute (1971). This implies a potential for removal by adsorption from water for 1,2-dichloropropane. Additionally, a log soil/water partition coefficient of 1.81 can be calculated based on the method of Briggs (1973); this further indicates a potential for adsorptive transport, although data are lacking in this area. To whatever extent this compound is adsorbed by clay, the importance of hydrolysis will increase.

54.4.6 Bioaccumulation

No specific data on bioaccumulation of this chemical were found. Here, again, the sizeable partition coefficients may indicate some potential for bioaccumulation.

54.4.7 Biotransformation and Biodegradation

1,2-Dichloropropane can be used as a carbon source by several soil bacteria at concentrations up to 1,000 mg/l (Altman and Lawlor 1966). Biodegradation is also thought to occur in sewage treatment facilities (Thom and Agg 1975). According to Roberts and Stoydin (1976), biodegradation in soil is very slow compared to volatilization.

54.5 Data Summary

The aquatic fate data for 1,2-dichloropropane are summarized in Table 54-1. The most important aquatic fate process for this compound is probably hydrolysis, and tropospheric photooxidation by hydroxyl radicals is probably also important.

Table 54-1

Summary of Aquatic Fate of 1,2-Dichloropropane

Environmental Process[a]	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	No data found.	-	-	Low
Oxidation	No data found; photooxidation in the troposphere is probably important.	-	-	Low
Hydrolysis	No specific data found; probably important.	-	0.5 - 2 years[b]	Low
Volatilization	Compound is volatile, but may return to the aquatic environment through precipitation.	-	Less than 1 hour to several hours[b]	Low
Sorption	No data found; may be adsorbed moderately.	-	-	Low
Bioaccumulation	No data found; may bioaccumulate slightly.	-	-	Low
Biotransformation/ Biodegradation	Biodegradation occurs slowly.	-	-	Low

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. Estimated from results of Dilling et al. (1975) with more highly chlorinated propanes.

54.6 Literature Cited

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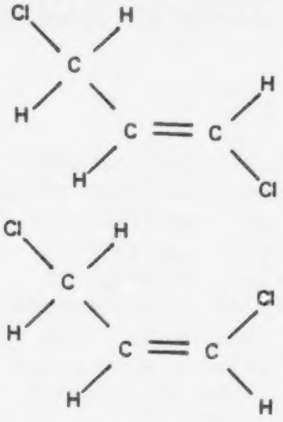
55. 1,3-DICHLOROPROPENE

55.1 Statement of Probable Fate

1,3-Dichloropropene is sufficiently volatile to be transported into the atmosphere as a vapor. It is expected that the compound will be photooxidized by hydroxyl radicals in the troposphere. 1,3-Dichloropropene is hydrolyzed in the environment to 3-chloroallyl alcohol.

55.2 Identification

1,3-Dichloropropene has been detected in finished drinking water (Shackelford and Keith 1976). The chemical structure of 1,3-dichloropropene is shown below.



(TRANS ISOMER)

(CIS ISOMER)

1,3-Dichloropropene

CAS NO. 542-75-6
TSL NO. UC 83100

Alternate Names

1,3-Dichloropropylene

55.3 Physical Properties

The general physical properties of 1,3-dichloropropene are as follows.

Molecular weight (Windholz 1976)	110.98
Melting point	No data found
Boiling point at 760 torr (Weast 1977)	104.3°C (cis isomer) 112°C (trans isomer)

Vapor pressure at 20°C (Dreisbach 1952)	25 torr
Solubility in water at 25°C (Dilling 1977)	2700 mg/l (cis isomer) 2800 mg/l (trans isomer)
Log octanol/water partition coefficient (Calc. by method of Tute 1971)	1.98

55.4 Summary of Fate Data

55.4.1 Photolysis

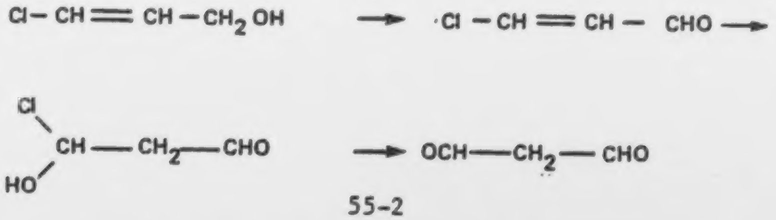
No data were found on the photolysis of this compound in water. Based on the data of Dilling *et al*. (1975), direct photolysis is relatively slow for chlorinated ethenes; presumably, this should also be the case for chlorinated propenes.

55.4.2 Oxidation

No specific data were found on oxidation of 1,3-dichloropropene. The work of Dilling *et al*. (1975) with chloroethenes indicated that oxidation of these compounds is typically not as important as volatilization or hydrolysis. This also may be true of 1,3-dichloropropene. Atmospheric oxidation, however, may be important after volatilization, although no specific information pertaining to this compound was found. Chlorinated ethenes are photooxidized relatively rapidly in the troposphere; Yung *et al*. (1975) report a tropospheric lifetime for trichloroethene with respect to reaction with hydroxyl radicals of about four days. The lifetime of 1,3-dichloropropene may be similarly short.

55.4.3 Hydrolysis

Dilling *et al*. (1975) determined half-lives with respect to hydrolysis of 10.7 months for trichloroethylene and 8.8 months for tetrachloroethylene, both chlorinated alkenes. Analogously, the half-life of hydrolysis for 1,3-dichloropropene should be at least several months. This conclusion agrees well with the first-order rate for hydrolysis of 1,3-dichloropropene in soil of 0.01 sec^{-1} to 0.035 sec^{-1} reported by Leistra (1970), which corresponds to a half-life of 20-70 days. The product of this hydrolysis reaction is the corresponding 3-chloroallyl alcohol, a potent biocide (Belser and Castro 1971). The 3-chloroallyl alcohol is probably degraded further to 3-chloroacrolein, which can then undergo hydrolysis to malondialdehyde as shown below. Oxidation of the dialdehyde produces malonic acid, a metabolic intermediate of many different food-chains.



55.4.4 Volatilization

According to Dilling et al. (1975), the evaporative half-life of 1,3-dichloropropene, originally present at 1 mg/l in water in a stirred container, was determined to be 31 minutes (both cis and trans isomers present). Loss of 90 percent required 98 minutes. This behavior is consistent with the reported vapor pressure of this material. Dilling et al. (1975) have pointed out the difficulty in extrapolating their laboratory data to environmental conditions, but the evaporative half-life in the environment is expected to be on the order of one-half hour to several hours, depending on conditions.

55.4.5 Sorption

When 1,3-dichloropropene is applied as a soil fumigant, it is readily adsorbed and persists for long periods of time (Leistra 1970; Thomason and McKenry 1973). In many cases, the adsorption of 1,3-dichloropropene is proportional to the content of organic matter in the soil (Leistra 1970). Degradation rates can be variable, but dissappearance generally is more rapid in clay soils than in sandy ones (Van Dijk 1973). The products of abiotic hydrolysis in moist soil and in water are the corresponding cis- and trans-3-chloroallyl alcohols (Castro and Belser 1966). It is very likely that base-catalyzed hydrolysis on the clay surface facilitates the formation of these products. The relative importance of adsorption as an aquatic fate process cannot be ascertained from the reviewed literature.

55.4.6 Bioaccumulation

Based on a calculated value for log octanol/water partition coefficient of 1.98, using the method of Tute (1971), bioaccumulation of this compound may be possible under conditions of chronic exposure. However, no experimental data concerning bioaccumulation were found.

55.4.7 Biotransformation and Biodegradation

Biodegradation of this compound does occur, according to Belser and Castro (1971) and Altman and Lawlor (1966). Belser and Castro (1971) studied the microbiological metabolism of the toxic hydrolysis product, 3-chloroallyl alcohol. Altman and Lawlor (1966) found that some soil bacteria can utilize 1,3-dichloropropene as a carbon source. Rates applicable to water were not found, but are expected to be slower than those for other removal processes.

55.5 Data Summary

The aquatic fate data, reported above for 1,3-dichloropropene, are summarized on Table 55-1. The primary transport process for removal from the aquatic environment appears to be volatilization. Once in the troposphere, 1,3-dichloropropene is probably readily attacked by hydroxyl radicals, and this photooxidation process appears to be the predominant fate of the compound. Hydrolysis may also be of importance as a fate process in aquatic systems.

Table 55-1

Summary of Aquatic Fate of 1,3-Dichloropropene

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	No data found.	-	-	Low
Oxidation[a]	Tropospheric photooxidation is probably the predominant fate process.	-	-	Medium
Hydrolysis	Appears to be relatively slow, but may be important.	0.01-0.035 sec^{-1} in soil[b]	20-70 days[b]	Medium
Volatilization	Reasonably rapid process; primary transport process.	-	31 minutes[c]	Medium
Sorption	No specific data.	-	-	Low
Bioaccumulation	No data found; probably not important.	-	-	Low
Biotransformation/ Biodegradation	Occurs slowly.	-	-	Low

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a. The predominant environmental process which is thought to determine the fate of the compound.

b. Leistra (1970).

c. Dilling *et al*. (1975), using a stirred system.

55.6 Literature Cited

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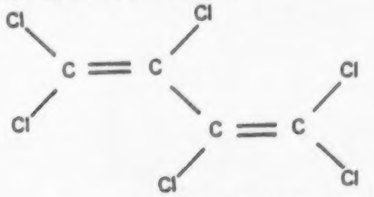
56. HEXACHLOROBUTADIENE

56.1 Statement of Probable Fate

Although the literature reviewed indicates that adsorption onto sediments is an important aquatic transport process for this compound, the potential contribution of bioaccumulation, volatilization, and quite possibly other processes, should not be discounted. Hexachlorobutadiene is a very persistent environmental pollutant. Its ultimate fate cannot, as yet, be determined.

56.2 Identification

Hexachlorobutadiene is present in domestic drinking water supplies (EPA 1975a), in aquatic organisms (EPA 1975b; Pearson and McConnell 1975; McConnell et al. 1975), in aquatic sediments (EPA 1975b; Pearson and McConnell 1975; McConnell et al. 1975), and is thought to be present in ambient waters as a significant by-product of production wastes from the manufacture of tetrachloroethene, trichloroethene, and tetrachloromethane (EPA 1975b). The chemical structure of hexachlorobutadiene is given below.



Hexachlorobutadiene

CAS NO. 87-68-3
TSL NO. EJ 07000

Alternate Names

HCBD
Hexachloro-1,3-butadiene

56.3 Physical Properties

The general physical properties of hexachlorobutadiene (HCBD) are as follows.

Molecular weight (Weast 1977)	260.76
Melting point (Weast 1977)	-21°C
Boiling point at 760 torr (Weast 1977)	215°C

Vapor pressure at 20°C (Pearson and McConnell 1975)	0.15 torr
Solubility in water at 20°C (Pearson and McConnell 1975)	2 mg/l
Log octanol/water partition coefficient (Calculated from method of Tute 1971)	3.74

56.4 Summary of Fate Data

56.4.1 Photolysis

Although the absorption spectrum of hexachlorobutadiene extends into the electromagnetic spectrum of sunlight, the absorption coefficient in this spectral region may be insufficient to make direct photolysis an important aquatic fate. A study by the Environmental Protection Agency (1976) showed that photolysis of hexachlorobutadiene in benzene yielded numerous products with a molecular weight higher than HCBD in quantities greater than the initial amount of HCBD present. This occurred after 15 minutes of irradiation at a wavelength of 273 nm. It was not apparent, however, whether HCBD was being photoactivated directly.

56.4.2 Oxidation

No information was found in the reviewed literature which pertains specifically to the oxidation of hexachlorobutadiene. Perhalogenated hydrocarbons are typically very stable with respect to oxidation.

56.4.3 Hydrolysis

No information was found in the reviewed literature pertaining specifically to the hydrolysis of hexachlorobutadiene. If hydrolysis of HCBD takes place on the clay surfaces of recently deposited sediments, the first expected product would be a chlorinated butenoic acid, based on results of studies by Roedig and Bernemann (1956) on solvolysis of HCBD in ethanol.

56.4.4 Volatilization

Unlike most short chain halogenated aliphatics, hexachlorobutadiene has a low vapor pressure and, thus, may not volatilize rapidly from the aqueous environment to the atmosphere. Hexachlorobutadiene has been reported to be present in domestic drinking water supplies in low concentrations (EPA 1975a) and has been detected at concentrations of 1.9 and 4.7 µg/l in water at two areas near Geismar, Louisiana. These concentrations indicate that HCBD may be quite persistent in natural waters. However, hexachloroethane, which is structurally somewhat similar to HCBD and exhibits a vapor pressure of 0.4 torr at 20°C (Verschueren 1977) in comparison to 0.15 torr for HCBD (Pearson and McConnell 1975), appears to be volatilized rather rapidly from water. Dilling (1977) determined a volatilization half-life in water of 40.7 minutes for hexachloroethane initially present at 0.72 mg/l in an open system stirred constantly at 200 rpm. Although no specific rate data were found for HCBD, volatilization may be an important transport process for this compound in aqueous systems.

56.4.5 Sorption

The currently reviewed literature contains an appreciable amount of information pertaining specifically to the adsorption of HCBD onto sediments. In a study of the Mississippi Delta region it was found that the level of hexachlorobutadiene in water was less than 2 μg/l while the concentration of hexachlorobutadiene in mud or soil samples exceeded 200 μg/l (EPA 1976). In this same study, water samples from the waste of an industrial company in Geismar, Louisiana, was found to contain from <0.1 μg/l to 4.5 μg/l HCBD. Levels of HCBD in the mud, however, reached a maximum of 2,370 μg/l, indicating selective concentration of several orders of magnitude. Leeuwangh et al. (1975) found that the concentration of HCBD in uncontaminated sediment after equilibration with water that contained HCBD was a 100 x that found in the water.

Samples taken from Liverpool Bay (England) showed the presence of HCBD, but rarely at levels greater than one μg/l (Pearson and McConnell 1975). McConnell et al. (1975) noted that coarse gravels have little adsorptive capacity for chlorinated aliphatics, whereas sediments rich in organic detritus have a much higher adsorptive capacity. The calculated log P (octanol/water partition coefficient) of 3.74 implies that hexachlorobutadiene should be strongly adsorbed by humus material.

56.4.6 Bioaccumulation

According to Kopperman et al. (1976) polar compounds are more easily biodegraded, whereas non-polar compounds tend to accumulate. The log octanol/water partition coefficient (log P) of 3.74, which was calculated using the method of Tute (1971), indicates that HCBD may bioaccumulate significantly.

Results of a study conducted for the Environmental Protection Agency (1976) showed that HCBD did not accumulate to high levels in test animals and that rates of uptake, as well as distribution in organs, were irregular. A flow-through system was used to determine accumulation of the compounds by algae and sediment. Concentration factors remained below 300 for both during relatively short-term experiments. A food-chain study compared the relative accumulation effects on a predator feeding upon HCBD-contaminated food-fish and a similar predator taking up the compound both through its food and through contaminated water. Uptake of HCBD was erratic. These laborarory experiments were compared with patterns of accumulation under field conditions. HCBD-free crayfish were caged, placed at a contaminated field site, and removed periodically for GC analysis. HCBD was not concentrated to a great extent and was accumulated irregularly. Concentration factors for crayfish left in the field site for 17 days ranged from 7.8 to 300 (33.7 to 1,290.3 μg/l HCBD).

56.4.7 Biotransformation and Biodegradation

No information was found in the currently reviewed literature pertaining specifically to the biodegradation of HCBD.

56.5 Data Summary

A summary of the aquatic fate information discussed above for HCBD is presented on Table 56-1. It appears that adsorption onto sediments is an important transport process and that bioaccumulation and volatilization may occur as well. The ultimate fate of HCBD cannot, as yet, be determined.

Table 56-1

Summary of Aquatic Fate of Hexachlorobutadiene

Environmental Process[a]	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	HCBD does not strongly absorb light above 290 nm; probably not important.	-	-	Low
Oxidation	No information found in reviewed literature.	-	-	Low
Hydrolysis	No information found in reviewed literature.	-	-	Low
Volatilization	May be important.	-	-	Low
Sorption	Selective concentration onto sediments has been demonstrated.	-	-	Medium
Bioaccumulation	Accumulation factors of the order of 1000 times have been reported; however, significant biomagnification or food-chain concentration has not been shown.	-	-	Medium
Biotransformation/ Biodegradation	No information found in reviewed literature.	-	-	Low

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

56.6 Literature Cited

Dilling, W.L. 1977. Interphase transfer processes. II. Evaporation rates of chloromethanes, ethanes, ethylenes, propanes, and propylenes from dilute aqueous solutions. Comparisons with theoretical predictions. Environ. Sci. Technol. 11:405-409.

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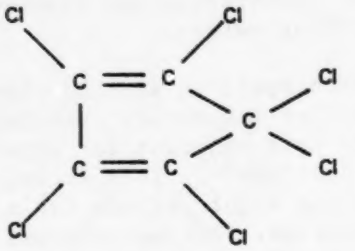
57. HEXACHLOROCYCLOPENTADIENE

57.1 Statement of Probable Fate

Several transport and fate processes appear to operate at significant rates to remove hexachlorocyclopentadiene from aquatic systems. The relative importance of these processes is thought to depend strongly on the characteristics of the individual water body, so that there is no clear indication that one process is predominant on an overall basis. The most important fate processes appear to be hydrolysis and near-surface photolysis, while transport occurs via the water column (as dissolved species), by volatilization to the atmosphere, and through adsorption onto particulates (perhaps to a lesser extent). The fate of HCCPD in the troposphere is not known.

57.2 Identification

Hexachlorocyclopentadiene has been detected in industrial effluents (Shackelford and Keith 1976). The chemical structure of hexachlorocyclopentadiene is shown below.



Alternate Names

HCCPD
Perchlorocyclopentadiene
Hex

Hexachlorocyclopentadiene

CAS NO. 77-47-4
TSL NO. GY 12250

57.3 Physical Properties

The general physical properties of hexachlorocyclopentadiene are as follows:

Molecular weight (Weast 1977)	272.77
Melting point (Weast 1977)	-9.9°C

Boiling point (Weast 1977)	239°C
Vapor pressure at 25°C (Ungnade and McBee 1957)	0.081 torr
Solubility in water (Lu et al. 1975)	0.805 mg/l
(Zepp et al. 1979)	1.8 mg/l (25°C)
Log octanol/water partition coefficient (Zepp et al. 1979)	3.99

57.4 Summary of Fate Data

57.4.1 Photolysis

Zepp *et al.* (1979) conducted photolysis experiments with hexachlorocyclopentadiene (HCCPD) in distilled water which utilized a variety of solar conditions. The compound was found to be highly photoreactive, exhibiting near-surface half-lives of less than ten minutes in all experiments. Photolysis rate constants were also determined for HCCPD in Aucilla (Fla.) River water, the results indicating that photosensitized reactions, as well as direct photolysis, occurred in the river water.

From the above data, plus the absorption spectrum and the photolytic reaction quantum efficiency from controlled laboratory experiments, Zepp *et al.* (1979) computed a mean near-surface rate constant for direct photolysis of HCCPD at 40°N latitude of about 3.9 hour^{-1}. This value, which was obtained by averaging over both dark and light periods for a year, corresponds to a half-life of about 11 minutes. Through the use of a mathematical model to predict behavior of organic chemicals in various types of water bodies, Zepp *et al.* (1979) conclude that photolysis is the predominant fate process for HCCPD in ponds and eutrophic lakes but not in turbid rivers.

Zepp *et al.* (1979) indicate that tetrachlorocyclopentadienone (TCPD), a highly reactive compound, is the primary photoproduct of HCCPD in water and it is likely to exist predominately in the hydrated form in the aquatic environment.

57.4.2 Oxidation

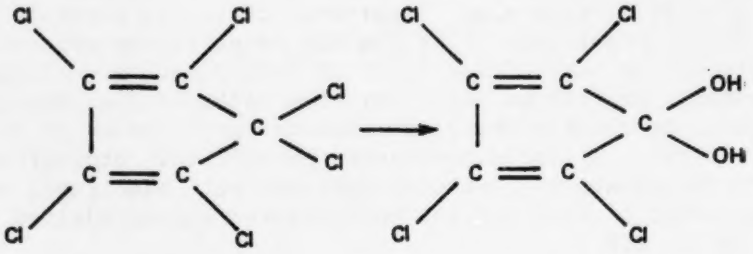
No information specifically concerning oxidation of HCCPD was found in the reviewed literature. Zepp *et al.* (1979) reported evidence of photosensitized reaction of HCCPD in natural waters which may have been photooxidation.

57.4.3 Hydrolysis

Hydrolysis rate constants for hexachlorocyclopentadiene at several temperatures and pH values were determined by Zepp et al. (1979). The reaction, in both distilled and natural water samples, was found to be independent of pH over the range 5 to 9 and dependent on temperature according to:

$$k_{obs} = 5.85 \times 10^{11} \exp(-2.460 \times 10^{4}/RT).$$

From the equation, the hydrolysis rate constant at 25°C is $5.6 \times 10^{-7} sec^{-1}$, corresponding to a half-life of 14 days. Hydrolysis of HCCPD adsorbed onto natural pond sediments was found to be at least as rapid as in the water. Acid catalyzed hydrolysis of HCCPD leads to tetrachlorocyclopentadienone hydrate (Ungnade and McBee 1957):



57.4.4 Volatilization

Zepp et al. (1979) determined the ratio of the volatilization rate to the reaeration rate constant for HCCPD in natural waters to be 0.58. The experimental method used was that described by Hill et al. (1976). This ratio was then utilized in a mathematical model to indicate relative importance of volatilization and other processes in the transport and fate of HCCPD in several types of aquatic systems. The results indicated that on the order of 15 percent of the HCCPD load in a turbid river would be removed by volatilization, as compared to less than five percent for a pond or a eutrophic lake.

57.4.5 Sorption

The log octanol/water partition coefficient of 3.99 (Zepp et al. 1979) indicates that adsorption of hexachlorocyclopentadiene onto organic-laden sediments may be appreciable. HCCPD held in sediments may be hydrolyzed or biodegraded; according to Zepp et al. (1979), hydrolysis is the more important process. The results obtained by Zepp et al. (1979), from analysis of HCCPD transport and fate by means of a mathematical model, indicate that sorption is not as important for this compound as competing processes.

57.4.6 Bioaccumulation

In a model ecosystem studied by Lu et al. (1975), hexachlorocyclopentadiene demonstrated bioaccumulation in all test organisms, ecological magnification (or EM) factors were as follows: algae 340; snail 929; mosquito 1634; fish 448.

57.4.7 Biotransformation and Biodegradation

The extent to which their test organisms were capable of biodegrading hexachlorocyclopentadiene in a model aquatic ecosystem was estimated by Lu et al. (1975) as: alga, 4 percent; snail, 10 percent; mosquito, 2 percent; fish, 27 percent. (The figures refer to the percentage of radioactivity present as metabolized HCCPD in comparison to unchanged HCCPD within the organism) Insofar as perchlorinated carbon-carbon double bonds are inert to biotic or abiotic oxidation, the primary product of biodegradation is probably tetrachlorocyclopentadienone hydrate. Biological detoxification of the hydrate by compound formation with glucuronic acid or oligosaccharides could account for the unidentified biodegradation products reported by Lu et al. (1975).

The results of Zepp et al. (1979), from the study of HCCPD by a mathematical model of fate and transport processes, indicate that biodegradation is probably not an important fate of this compound, in that one percent or less of HCCPD in aquatic systems was predicted to be microbially transformed.

57.5 Data Summary

The data on the environmental fate of HCCPD are summarized in Table 57-1 . Near-surface photolysis and hydrolysis (both in the water column and in sediments) appear to be important fate processes for HCCPD. Transport can occur by volatilization, as dissolved species in the water column, and through adsorption onto particulates (perhaps to a lesser extent).

According to Zepp _et al_. (1979) the relative importance of these processes depends strongly on the characteristics of the individual aquatic system. Their analysis indicates that photolysis is predominant in ponds and lakes, but that water-borne export and volatilization are each more important than photolysis in a turbid river.

Because a number of aquatic transport and fate processes appear to compete, in the case of HCCPD, and because the accuracy of the method used by Zepp _et al_. (1979) to mathematically analyze them has not been verified, a single predominant fate process cannot be selected at this time.

Table 57-1

Summary of Aquatic Fate of Hexachlorocyclopentadiene

Environmental Process[a]	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Near-surface photolysis is an important process.	4.9 day^{-1}	11 minutes	Medium
Oxidation	No specific data available; photooxidation in aquatic systems may occur.	-	-	Low
Hydrolysis	Appears to be an important fate process.	$5.6 \times 10^{-7} \text{sec}^{-1}$ at $25^\circ C$	14 days	Medium
Volatilization	Appears to be important in flowing waters.	-	-	Medium
Sorption	Should be significant although no specific environmental data are available.	-	-	Low
Bioaccumulation	May be significant for some biological systems.	-	-	Medium
Biotransformation/ Biodegradation	Does not appear to be an important fate process.	-	-	Low

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[a] There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

57.5 Literature Cited

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58. BROMOMETHANE (METHYL BROMIDE)

58.1 Statement of Probable Fate

The two most probable fates of bromomethane in the environment are photooxidation in the troposphere and hydrolysis in the aquatic environment.

Volatilization is the major transport process of bromomethane from aquatic systems. Once in the troposphere, bromomethane reacts with hydroxyl radicals to form bromine atoms and inorganic bromides, which may return to earth during the precipitation process. Any unreacted portion of bromomethane which diffuses upward to the stratosphere would be expected to undergo significant photodissociation.

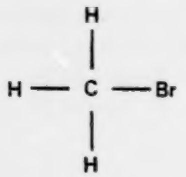
A maximum hydrolytic half-life of 20 days has been reported for bromomethane at pH 7 and 25°C. As a result, hydrolysis may serve as an important fate of this compound.

Based on the information found, it appears that oxidation is not an important fate process of bromomethane in the aquatic environment. In addition, the literature reviewed contained no specific information indicating that biodegradation, adsorption, and bioaccumulation are important processes for this chemical in the aquatic environment.

58.2 Identification

Bromomethane may be ubiquitous in the environment due to natural as well as anthropogenic sources. Its presence has been detected in finished drinking water (Environmental Protection Agency 1975), in seawater (Lovelock 1975; Singh et al. 1978), and in the troposphere (Singh et al. 1978).

The chemical structure of bromomethane is shown below.



Bromomethane

CAS NO. 74-83-9
TSL NO. PA 49000

Alternate Names

Methyl bromide
Terabol
Monobromomethane
Embafume

58.3 Physical Properties

The general physical properties of bromomethane are given below.

Molecular weight (Weast 1977)	94.94
Melting point (Weast 1977)	-93.6°C
Boiling point at 760 torr (Verschueren 1977)	4.6°C
Vapor pressure at 20°C (Environmental Protection Agency 1976)	1420 torr
Solubility in water at 20°C (Verschueren 1977)	900 mg/l
Log octanol/water partition coefficient (Calculated from Tute 1971, See Methods Section on Bioaccumulation)	1.1

58.4 Summary of Fate Data

58.4.1 Photolysis

No information was found pertaining to the photolysis of bromomethane in the aqueous environment. Due to the high vapor pressure of bromomethane, volatilization to the atmosphere is quite rapid. The dominant loss mechanism for bromomethane from the lower troposphere is said to be upward diffusion (Robbins 1976). Bromomethane is not known to undergo significant light absorption at wavelengths above 290 nm (Robbins 1976). As a result, photodissociation cannot play an important role in the loss of bromomethane below the ozone layer since the ozone layer effectively absorbs wavelengths of light less than 290 nm (Hanst 1978). The wavelength region in which significant photodissociation in the stratosphere occurs is from about 180 to 240 nm (Robbins 1976). That portion of bromomethane which diffuses upward to the stratosphere would be expected to undergo significant photodissociation.

58.4.2 Oxidation

No information was found pertaining specifically to the oxidation of bromomethane in the aqueous environment under ambient conditions. According to Radding et al. (1977), oxidation of alkyl halides in water by RO radical is not significant, having a half-life of greater than 100 years.

In the upper troposphere and lower stratosphere loss of bromomethane occurs by reaction with hydroxyl radicals (Robbins 1976). Wofsy et al. (1975) contend that bromomethane is removed as follows:

$$\cdot OH + CH_3Br \longrightarrow H_2O + \cdot CH_2Br$$

The bromine atom is subsequently released and inorganic bromide is reported to be carried out of the lower atmosphere by rain (Wofsy et al. 1975). The rate constant for the above reaction is reported to be $2 \times 10^{-12} cm^3 molecule^{-1} sec^{-1}$ exp (-1200/T). By substituting 300°K (27°C) for T, a bimolecular rate of 3.6×10^{-14} $cm^3 sec^{-1}$ is obtained for reaction of bromomethane with hydroxyl radicals at 27°C.

The photooxidation rate data of Wofsy et al. indicates a tropospheric lifetime (1/k) on the order of one year for bromomethane. Assuming a troposphere-to-stratosphere turnover time (time required for all but 1/e of tropospheric air to diffuse into the stratosphere) of 30 years, about three percent of tropospheric bromomethane would be expected to eventually reach the stratosphere.

58.4.3 Hydrolysis

A maximum hydrolytic half-life of 20 days has been reported for bromomethane at pH 7 and 25°C (Mabey and Mill 1978; Radding et al. 1977). This corresponds to a first order rate constant for hydrolysis of bromomethane of $4.0 \times 10^{-7} sec^{-1}$ (Mabey and Mill 1978; Radding et al. 1977). The short hydrolytic half-life of bromomethane makes it likely that hydrolysis is an important fate process for this compound.

58.4.4 Volatilization

Volatilization is the dominant process for the removal of bromomethane from the aqueous environment. Although no rates for volatilization of bromomethane were found, one can extrapolate information from its more thoroughly studied analogue, chloromethane, and other halogenated aliphatics. Dilling et al. (1975) estimated the experimental half-life for volatilization of chloromethane originally present at 1 mg/l to be 27 minutes when stirred at 200 rpm in water at approximately 25°C in an open container. Removal of 90 percent of the chloromethane under the same conditions required 91 minutes. For chloroaliphatics in general, stirring speed was found to have a marked effect on volatilization rate. With no stirring except 15 seconds every five minutes, the time required for 50 percent depletion of trichloromethane, trichloroethene, and 1,1,1-trichloroethane, compounds similar to chloromethane, was greater than 90 minutes or on the order of from times greater than the stirred case for these compounds.

Dilling et al. (1975) are careful to point out the difficulties encountered in extrapolating their laboratory results to real-world conditions, where the concentration of the organic solute would probably be very much less than 1 mg/l and where surface and bulk agitation would be highly variable. Although the data appear to be valid on a relative basis (i.e., correctly illustrating the relative rates of volatilization of chlorinated aliphatics), they cannot be used as absolute measures of volatilization rates from natural waters. For the purposes of this document, the data are used as rough-order-of-magnitude indications of the importance of volatilization relative to other transport and fate processes, with the strong effects of agitation considered. The validity of this application has not been established.

58.4.5 Sorption

No data pertaining to adsorption of bromomethane onto sediments were found. Since bromomethane volatilizes rapidly from the aqueous environment, it is unlikely that adsorption onto sediment is a significant transport process for this chemical.

58.4.6 Bioaccumulation

The log octanol/water partition coefficient (log P) for bromomethane is 1.10 (calculated from Tute 1971), indicating that bromomethane is not very lipophilic and, thus, probably does not exhibit a significant tendency to bioaccumulate in organisms. Laboratory animals given doses of bromomethane have demonstrated no indications of significant accumulation of the compound (Environmental Protection Agency 1976). In addition, there has been no indication of significant accumulation in soils from annual application (Environmental Protection Agency 1976).

58.4.7 Biotransformation and Biodegradation

No data were found pertaining to biological degradation of bromomethane by aquatic organisms.

58.5 Data Summary

Table 58-1 summarizes the aquatic fate of bromomethane. The oxidation rate is a photooxidation rate and refers to the rate of reaction of bromomethane with hydroxyl radicals in the troposphere. The two most likely fates of bromomethane in the environment are photooxidation in the troposphere and aquatic hydrolysis.

Table 58-1

Summary of Aquatic Fate of Bromomethane

Environmental Process[a]	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Probably not significant in aquatic systems.	-	-	Medium
Oxidation	An important fate of this compound is attack by hydroxyl radicals in the troposphere.	$3.6 \times 10^{-14} cm^3 sec^{-1}$	~1 year[b]	High
Hydrolysis	Probably a significant fate process.	$4.0 \times 10^{-7} sec^{-1}$[c]	20 days	High
Volatilization	Primary transport process from the aquatic environment.	-	-	Medium
Sorption	Probably not significant.	-	-	Low
Bioaccumulation	Probably does not significantly bioaccumulate in organisms.	-	-	Medium
Biotransformation/ Biodegradation	Biodegradation is probably not a significant fate and occurs at a slow rate.	-	-	Low

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. Estimated from rate.

c. The hydrolysis rate is a maximum rate.

58.6 Literature Cited

Dilling, W.L., N.B. Tefertiller, and G.J. Kallos. 1975. Evaporation rates of methylene chloride, chloroform, 1,1,1-trichloromethane, trichloroethylene, tetrachloroethylene and other chlorinated compounds in dilute aqueous solutions. Environ. Sci. Technol. 9(9):833-838.

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Lovelock, J.E. 1975. Natural halocarbons in the air and in the sea. Nature 256:193-194.

Mabey, W. and T. Mill. 1978. Critical review of hydrolysis of organic compounds in water under environmental conditions. J. Phys. Chem. Ref. Data 7(2):383-415.

Radding, S.B., D.H. Liu, H.L. Johnson, and T. Mill. 1977. Review of the environmental fate of selected chemicals. Environmental Protection Agency (Office of Toxic Substances), Washington, D.C. 147p. EPA 560/5-77-003.

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Singh, H.B., L.J. Salas, H. Shiegeishi, and A.H. Smith. 1978. Fate of halogenated compounds in the atmosphere interim report - 1977. Environmental Protection Agency (Office of Research and Development), Research Triangle Park, N.C. 57p. EPA 600/3-78-017.

Tute, M.S. 1971. Principles and practice of Hansch analysis: A guide to structure-activity correlation for the medicinal chemist. Adv. Drug Res. 6:1-77.

Verschueren, K. 1977. Handbook of environmental data on organic chemicals. Van Nostrand/Reinhold Press, New York. 659p.

Weast, R.C. (ed.). 1977. Handbook of chemistry and physics. 58th Edition. CRC Press, Cleveland, Ohio. 2398p.

Wofsy, S.C., M.B. McElroy, and Y.L. Yung. 1975. The chemistry of atmospheric bromine. Geophys. Res. Lett. 2(6):215-218.

59. BROMODICHLOROMETHANE

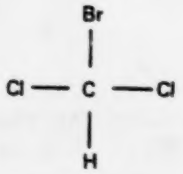
59.1 Statement of Probable Fate

The information found is not sufficient to determine the aquatic fate of bromodichloromethane.

59.2 Identification

Bromodichloromethane has been detected in finished drinking water (Kleopfer and Fairless 1972; Environmental Protection Agency 1975), and in sources of drinking water (Environmental Protection Agency 1975). Bromodichloromethane is hypothesized to be present in water supplies as a result of the haloform reaction which occurs during the chlorination of such water (Rook 1974; Environmental Protection Agency 1975; Glaze and Henderson 1975).

The chemical structure of bromodichloromethane is shown below.



$$\begin{array}{c} \mathrm{Br} \\ | \\ \mathrm{Cl} - \mathrm{C} - \mathrm{Cl} \\ | \\ \mathrm{H} \end{array}$$

Alternate Names
Dichlorobromomethane

Bromodichloromethane

CAS NO. 75-27-4
TSL NO. Not Assigned

59.3 Physical Properties

The general physical properties of bromodichloromethane are given below.

Molecular weight (Weast 1977)	163.83
Melting point (Weast 1977)	-57.1°C
Boiling point at 760 torr (Weast 1977)	90°C
Vapor pressure at 20°C (Dreisbach 1952)	50 torr

Solubility in water	Not available
Log octanol/water partition coefficient (Calculated from Tute 1971, See Methods Section on Bioaccumulation)	1.88

59.4 Summary of Fate Data

59.4.1 Photolysis

No information was found pertaining specifically to the rate of photolysis of bromodichloromethane in either the aquatic or atmospheric environments.

59.4.2 Oxidation

No information was found pertaining specifically to the rate of oxidation of bromodichloromethane in the aquatic environment. Bromodichloromethane is probably like other halogenated aliphatics in that it is not easily oxidized in aquatic systems since there are no functional groups which react strongly with hydroxyl radicals.

59.4.3 Hydrolysis

A maximum hydrolytic half-life of 137 years has been reported for bromodichloromethane at pH 7 and 25°C (Mabey and Mill 1978). This corresponds to a first-order rate constant for hydrolysis of bromodichloromethane of $1.6 \times 10^{-10} sec^{-1}$ (Mabey and Mill 1978).

59.4.4 Volatilization

No information was found pertaining specifically to the rate of volatilization of bromodichloromethane from water. Volatilization may very well be an important transport process for bromodichloromethane from water to the atmosphere. It must be noted, however, that the vapor pressure of bromodichloromethane is much lower than that for chloroform and other chloroalkanes. As a result, bromodichloromethane would not be expected to volatilize as rapidly as chlorinated methanes such as chloroform. The concentration of bromodichloromethane present in water supplies has been reported to decrease as a result of volatilization while flowing through open channels (Rook 1974).

59.4.5 Sorption

No information was found pertaining specifically to the adsorption of bromodichloromethane onto suspended sediments. The concentration of bromodichloromethane produced by chlorination can be reduced by treatment of the water with powdered activated carbon (Rook 1974).

59.4.6 Bioaccumulation

Neely et al. (1974) have shown that bioaccumulation is directly related to the octanol/water partition coefficient (P) of the compound. The log octanol/water partition coefficient (log P) as calculated by the method of Hansch is 1.88 (Tute 1971) indicating that bromodichloromethane is somewhat lipophilic (see Methods section on bioaccumulation). As a result, bioaccumulation in organisms may be possible for this compound. No information was found, however, reporting the bioaccumulation of bromodichloromethane in organisms.

59.4.7 Biotransformation and Biodegradation

No information was found pertaining specifically to the biodegradation of bromodichloromethane. In the sea, many species of brown seaweed, molluscs, sponges, and bacteria metabolize halogens (Anonymous 1977). The red algae, or Rhodophyta, are known to use mostly bromine and they also synthesize several different organic substances, some containing iodine and chlorine.

59.4.8 Other Reactions

Rook (1977) suggests that bromodichloromethane, which has been found in finished drinking water, may be present in such chlorinated water due to the haloform reaction. The haloform reaction, connected with the chlorination of water supplies, occurs generally in alkaline solution with organic compounds containing the acetyl group or with structures that may be readily oxidized to the acetyl group (Morris 1975). The three hydrogens of the methyl component of the acetyl group are successively replaced by chlorine or other halogens, and subsequently the carbon bond to the carbonyl group is hydrolyzed giving rise to a haloform and a carboxylic acid (Morris 1975). The simplified reaction is given below using production of chloroform as an example:

$$CH_3COR + 3HOCl \longrightarrow CCl_3COR + 3H_2O \quad (1)$$
$$CCl_3COR + H_2O \longrightarrow CHCl_3 + RCOOH \quad (2)$$

It is suggested that organic compounds containing the acetyl group, needed for the haloform reaction to occur, are present in the form of humic materials which cause the yellow to brown coloration of surface waters (Rook 1974; Rook 1977; Morris 1975). For the most part humic materials have a molecular weight in the 10^4-10^5 range and fall into the group of compounds designated as fulvic acids (Rook 1977; Morris 1975).

There are several conditions which must be met in order for the haloform reaction to occur. These conditions are discussed below.

First, the haloform reaction generally occurs at pH of 5 or greater. Chlorine dispersed in water at pH greater than 5, as employed in water treatment in concentrations up to 100 mg/l or about 10^3 molar, is hydrolyzed instantly and entirely to HOCl and OCl^- (Morris 1975). The overall reactions are as follows:

$$Cl_2 + HCO_3^- \longrightarrow HOCl + Cl^- + CO_2$$
$$HOCl \rightleftharpoons H^+ + OCl^-$$

Thus, it is necessary to consider the reactions of hypochlorous acid rather than those of Cl_2 in describing the potential reactions of dilute aqueous chlorine with organic compounds.

Secondly, the haloform reaction must occur at sites on the fulvic acids which are the most conducive to the formation of haloforms. Although the carbon content of fulvic acid is about 50 percent, there are very few carbons which have the chemical constituents necessary for the haloform reaction to occur. It is for this reason that the yield of haloforms produced upon aqueous chlorination is fairly low (Rook 1977). The carbon between two meta positioned OH-groups of a hydroxylated aromatic ring is proposed as the most reactive site for haloform formation (Rook 1977).

The bromide ion, even at very low concentrations (as low as 0.1 mg/l), greatly influences chlorination reactions (Rook 1974; Morris 1975). Bromide is very rapidly oxidized to hypobromous acid by aqueous chlorine. The resulting HOBr reacts more rapidly and completely with organic matter than does HOCl (Morris 1975; Rook 1974). The bromide regenerated in the reduction of HOBr is readily reoxidized by excess HOCl and thus can serve as a catalyst in oxidation reactions (Morris 1975; Rook 1974).

59.5 Data Summary

Table 59-1 summarizes the aquatic fate data discussed above. The information found is insufficient to predict the aquatic fate of bromodichloromethane.

Table 59-1

Summary of Aquatic Fate of Bromodichloromethane

Environmental Process[a]	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	No information found	-	-	-
Oxidation	No information found	-	-	-
Hydrolysis	Is too slow to be a significant fate.	$1.6 \times 10^{-10} sec^{-1}$	137 years[b]	Medium
Volatilization	No specific information; probably serves as a significant transport process in water chlorination.	-	-	-
Sorption	No specific information; adsorption onto activated carbon probably serves as a significant process in water chlorination.	-	-	-
Bioaccumulation	According to the log P value obtained, this compound may bioaccumulate in organisms.	-	-	Low
Biotransformation/ Biodegradation	No specific information; in the sea, many invertebrates metabolize halogens.	-	-	-

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. The hydrolysis half-life is a maximum value.

59.6 Literature Cited

Anonymous. 1977. Man is not the only polluter. Environ. Sci. Technol. 11(5):442-443.

Dreisbach, R.R. 1952. Pressure-volume-temperature relationships of organic compounds. Handbook Publishers, Inc., Sandusky, Ohio. 135p.

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Glaze, W.H. and J.E. Henderson, IV. 1975. Formation of organochlorine compounds from the chlorination of a municipal secondary effluent. J. Water Pollut. Control Fed. 47:2511-2515.

Kleopfer, R.D. and B.J. Fairless. 1972. Characterization of organic components in a municipal water supply. Environ. Sci. Technol. 6(12): 1036-1037.

Mabey, W. and T. Mill. 1978. Critical review of hydrolysis of organic compounds in water under environmental conditions. Phys. Chem. Ref. Data 7(2):383-415.

Morris, J.C. 1975. Formation of halogenated organics by chlorination of water supplies. Environmental Protection Agency (Office of Research and Development) 54p. EPA-600/1-75-002.

Neely, W.B., D.R. Branson, and G.E. Blau. 1974. Partition coefficient to measure bioconcentration potential of organic chemicals in fish. Environ. Sci. Technol. 8(13):1113-1115.

Rook, J.J. 1974. Formation of haloforms during chlorination of natural waters. J. Soc. Water Treat. Exam. 23(Part 2):234-243.

Rook, J.J. 1977. Chlorination reactions of fulvic acids in natural waters. Environ. Sci. Technol. 11(5):478-482.

Tute, M.S. 1971. Principles and practices of Hansch analysis: a guide to structure-activity correlation for the medicinal chemist. Adv. Drug Res. 6:1-77.

Weast, R.C. (ed.). 1977. Handbook of chemistry and physics. 58th Edition. CRC Press, Cleveland, Ohio. 2398p.

60. DIBROMOCHLOROMETHANE

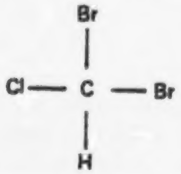
60.1 Statement of Probable Fate

Very little data on physical properties or reactions of dibromochloromethane were found in the literature. It is, therefore, not possible to determine the aquatic fate of dibromochloromethane at this time.

60.2 Identification

Dibromochloromethane has been detected in finished drinking water (Kleopfer and Fairless 1972; Environmental Protection Agency 1975), in drinking water supplies (Environmental Protection Agency 1975), and in wastewater effluents (Glaze and Henderson 1975). Dibromochloromethane is hypothesized to be present in water supplies as a result of the haloform reaction which takes place during the chlorination of such water (Rook 1974; Environmental Protection Agency 1975; Glaze and Henderson 1975).

The chemical structure of dibromochloromethane is shown below.



$$Cl-\overset{\overset{Br}{|}}{\underset{\underset{H}{|}}{C}}-Br$$

Dibromochloromethane

CAS NO. 124-48-1
TSL. NO. None Assigned

Alternate Names

Chlorodibromomethane

60.3 Physical Properties

The general physical properties of dibromochloromethane are as follows.

Molecular weight (Weast 1977)	208.29
Melting point (Verschueren 1977)	<-20°C
Boiling point at 748 torr (Weast 1977)	119-120°C
Vapor pressure at 10.5°C (Dreisbach 1952)	15 torr

Solubility in water	Not available
Log octanol/water partition coefficient (Calculated from Tute 1971, see Methods Section on Bioaccumulation)	2.09

60.4 Summary of Fate Data

60.4.1 Photolysis

No information was found pertaining to the rate of photolysis of dibromochloromethane in either the aquatic or atmospheric environments under ambient conditions.

60.4.2 Oxidation

No information was found pertaining to the rate of oxidation of dibromochloromethane in either the aquatic or atmospheric environments. Dibromochloromethane is probably like other halogenated aliphatics in that it is not easily oxidized in aquatic systems since there are no functional groups which react strongly with OH.

60.4.3 Hydrolysis

A maximum hydrolytic half-life of 274 years has been reported for dibromochloromethane at pH 7 and 25°C (Mabey and Mill 1978). This corresponds to a first-order rate constant for hydrolysis of dibromochloromethane of $8.0 \times 10^{-11} sec^{-1}$ (Mabey and Mill 1978).

60.4.4 Volatilization

No information was found pertaining specifically to the rate of volatilization of dibromochloromethane from water. Volatilization may be an important transport process for dibromochloromethane from water to the atmosphere. It must be noted, however, that the vapor pressure of dibromochloromethane is much lower than that for chloroform and other chloroalkanes. As a result, dibromochloromethane would not be expected to volatilize as rapidly as chlorinated methanes such as chloroform. The concentration of dibromochloromethane present in water supplies has, however, been reported to decrease as a result of volatilization while flowing through open channels (Rook 1974).

60.4.5 Sorption

No information was found pertaining specifically to the adsorption of dibromochloromethane onto suspended sediments. The concentration of dibromochloromethane produced by chlorination can be reduced by treatment of water containing this compound with powdered activated carbon (Rook 1974).

60.4.6 Bioaccumulation

Neely et al. (1974) have shown that bioaccumulation is directly related to the octanol/water partition coefficient (P) of the compound. The log octanol/water partition coefficient (log P) as calculated by the method of Hansch is 2.09 (Tute 1971) indicating that dibromochloromethane is somewhat lipophilic (see Methods section on bioaccumulation). As a result, dibromochloromethane may exhibit a tendency to bioaccumulate in organisms. No information was found, however, reporting the bioaccumulation of dibromochloromethane in organisms.

60.4.7 Biotransformation and Biodegradation

No information was found pertaining specifically to the biodegradation of dibromochloromethane. In the sea, many species of brown seaweed, molluscs, sponges, and bacteria metabolize halogens (Anonymous 1977). The red algae, or Rhodophyta, are known to use mostly bromine and they also synthesize several different organic substances, some containing iodine and chlorine.

60.4.8 Other Reactions

Rook (1977) suggested that dibromochloromethane, which has been found in finished drinking water, may be present in such chlorinated water due to the haloform reaction. The haloform reaction, connected with the treatment of water supplies, occurs generally in alkaline solution with organic compounds containing the acetyl group or with structures that may be readily oxidized to the acetyl group (Morris 1975). The three hydrogens of the methyl component of the acetyl group are successively replaced by chlorine or other halogen, and then the carbon bond to the carbonyl group is hydrolyzed giving rise to a haloform and a carboxylic acid (Morris 1975). The simplified reaction is given below using production of chloroform as an example:

$$CH_3COR + 3\ HOCl \longrightarrow CCl_3COR + 3\ H_2O \qquad (1)$$

$$CCl_3COR + H_2O \longrightarrow CHCl_3 + RCOOH \qquad (2)$$

It is suggested that organic compounds that have an acetyl group, needed for the haloform reaction to occur, are present in the form of humic materials which cause the yellow to brown coloration of surface waters (Rook 1974; Rook 1977; Morris 1975). For the most part humic materials have a molecular weight in the 10^4 - 10^5 range and fall into the group of compounds designated as fulvic acids (Rook 1977; Morris 1975).

There are several conditions which must be met in order for the haloform reaction to occur. These conditions are as follows.

First, the haloform reaction generally occurs at pH of 5 or greater. Chlorine dispersed in water at pH greater than 5, as employed in water treatment in concentrations up to 100 mg/l or about 10^3 molar, is hydrolyzed instantly and entirely to HOCl and OCl^- (Morris 1975). The overall reactions are as follows:

$$Cl_2 + HCO_3^- \longrightarrow HOCl + Cl + CO_2$$

$$HOCl \rightleftharpoons H^+ + OCl^-$$

Thus, it is necesasary to consider the reactions of hypochlorous acid rather than those of Cl_2 in describing the potential reactions of dilute aqueous chlorine with organic compounds.

Secondly, the haloform reaction must occur at sites on the fulvic acids which are the most conducive to the formation of haloforms. Although the carbon content of fulvic acid is about 50 percent, there are very few carbons which have the chemical constituents necessary for the haloform reaction to occur. It is for this reason that the yield of haloforms produced upon aqueous chlorination is fairly low (Rook 1977). The carbon between two meta positioned OH groups of a hydroxylated aromatic ring is proposed as the most reactive site for haloform formation (Rook 1977).

The bromide ion, even at very low concentrations (as low as 0.1 mg/l), greatly influences chlorination reactions (Rook 1974; Morris 1975). Bromide is very rapidly oxidized to hypobromous acid by aqueous chlorine. The resulting HOBr reacts more rapidly and completely with organic matter than does HOCl (Morris 1975; Rook 1974). The bromide regenerated in the reduction of HOBr is readily reoxidized by excess HOCl and thus can serve as a catalyst in oxidation reactions (Morris 1975; Rook 1974).

60.5 Data Summary

Table 60-1 summarizes the aquatic fate data discussed above. The information found is insufficient to predict the aquatic fate of dibromochloromethane.

Table 60-1

Summary of Aquatic Fate of Dibromochloromethane

Environmental Process[a]	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	No information.	-	-	-
Oxidation	No information.	-	-	-
Hydrolysis	Too slow to be a significant fate process.	$8.0x10^{-11} sec^{-1}$	274 years[b]	Medium
Volatilization	No specific information; probably serves as a significant transport process.	-	-	-
Sorption	No specific information; adsorption onto activated carbon probably serves as a significant process in water purification.	-	-	-
Bioaccumulation	According to the log P value obtained, this compound may bioaccumulate in organisms.	-	-	Low
Biotransformation/ Biodegradation	No specific information; in the sea, many invertebrates metabolize halogenated methanes.	-	-	-

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. Reported as a maximum hydrolytic half-life.

60.6 Literature Cited

Anonymous. 1977. Man is not the only polluter. Environ. Sci. Technol. 11(5):442-443.

Dreisbach, R.R. 1952. Pressure-volume-temperature relationships of organic compounds. Handbook Publishers, Inc. Sandusky, Ohio. 135p.

Environmental Protection Agency. 1975. Preliminary assessment of suspected carcinogens in drinking water. Environmental Protection Agency, (Office of Toxic Substances), Washington, D.C. 33p. EPA 560/4-75-003.

Glaze, W.H. and J.E. Henderson, IV. 1975. Formation of organochlorine compounds from the chlorination of a municipal secondary effluent. J. Water Pollut. Control. Fed. 47:2511-2515.

Kleopfer, R.D. and B.J. Fairless. 1972. Characterization of organic components in a municipal water supply. Environ. Sci. Technol. 6(12): 1036-1037.

Mabey, W. and T. Mill. 1978. Critical review of hydrolysis of organic compounds in water under environmental conditions. J. Phys. Chem. Ref. Data 7(2):383-415.

Morris, J.C. 1975. Formation of halogenated organics by chlorination of water supplies. Environmental Protection Agency (Office of Research and Development). 54p. EPA 600/1-75-002.

Neely, W.B., D.R. Branson, and G.E. Blau. 1974. Partition coefficient to measure bioconcentration potential of organic chemicals in fish. Environ. Sci. Technol. 8(13):1113-1115.

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Rook, J.J. 1977. Chlorination reactions of fulvic acids in natural waters. Environ. Sci. Technol. 11(5):478-482.

Tute, M.S. 1971. Principles and practices of Hansch analysis: a guide to structure-activity correlation for the medicinal chemist. Adv. Drug Res. 6:1-77.

Verschueren, K. 1977. Handbook of environmental data on organic chemicals. Van Nostrand/Reinhold Press, New York. 659p.

Weast, R.C. (ed.). 1977. Handbook of chemistry and physics. 58th Edition. CRC Press, Cleveland, Ohio. 2398p.

61. TRIBROMOMETHANE (BROMOFORM)

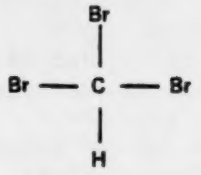
61.1 Statement of Probable Fate

The currently reviewed literature contains insufficient information to indicate the aquatic fate of tribromomethane.

61.2 Identification

Tribromomethane has been detected in finished drinking water (Kleopfer and Fairless 1972; Environmental Protection Agency 1975) and in drinking water supplies (Environmental Protection Agency 1975). Tribromomethane is hypothesized to be present in water supplies as a result of the haloform reaction which takes place during the chlorination of such water (Rook 1974; Environmental Protection Agency 1975; Glaze and Henderson 1975).

The chemical structure of tribromomethane is shown below.



$$\begin{array}{ccccc} & & Br & & \\ & & | & & \\ Br & - & C & - & Br \\ & & | & & \\ & & H & & \end{array}$$

Tribromomethane

CAS NO. 75-25-2
TSL NO. PB 56000

Alternate Names

Bromoform
Methenyl tribromide

61.3 Physical Properties

The general physical properties of tribromomethane are as follows.

Molecular weight (Weast 1977)	252.75
Melting point (Weast 1977)	8.3°C
Boiling point at 760 torr (Weast 1977)	149.5°C
Vapor pressure at 34°C (Weast 1977)	10 torr

Solubility in water (Seidell 1941)	3010 mg/l at 15°C 3190 mg/l at 30°C
Log octanol/water partition coefficient (Calculated from Tute 1971; see methods section on bioacccumulation)	2.30

61.4 Summary of Fate Data

61.4.1 Photolysis

No information pertaining to the rate of photolysis of tribromomethane in either the aquatic or atmospheric environments was found.

61.4.2 Oxidation

No information pertaining specifically to the rate of oxidation of tribromomethane in the aquatic environment was found. According to Radding et al. (1977), oxidation of tribromomethane by hydroxyl (OH·) radicals in the troposphere will be relatively rapid with a one or two month half-life. The photooxidation product of tribromomethane is likely to be $COBr_2$ which, in turn, may be removed by rain and be hydrolyzed to CO_2 and HBr (Radding et al. 1977). Assuming a troposphere-to-stratosphere turnover time (time for all but 1/e of tropospheric air to diffuse into the stratosphere) of 30 years, a tropospheric half-life of one or two months would result in less than one percent of tropospheric tribromomethane reaching the stratosphere.

61.4.3 Hydrolysis

A maximum hydrolytic half-life of 686 years has been estimated for tribromomethane at pH 7 and 25°C by extrapolation from experimental data at 100-150°C (Radding et al. 1977). This corresponds to a first-order rate constant for hydrolysis of tribromomethane of $3.2 \times 10^{-11} sec^{-1}$ (Radding et al. 1977; Mabey and Mill 1978).

61.4.4 Volatilization

No information pertaining specifically to the rate of volatilization of tribromomethane from water was found. Volatilization may very well be an important transport process for tribromomethane from water to the atmosphere. It must be noted, however, that the vapor pressure of tribromomethane is much lower than that for chloroform (trichloromethane) and many other chloroalkanes. As a result, tribromomethane would not be expected to volatilize as rapidly as chlorinated methanes. The concentration of tribromomethane present in water supplies has been reported to decrease, while flowing through open channels, as a result of volatilization (Rook 1974).

61.4.5 Sorption

No information pertaining to the adsorption of tribromomethane onto sediments was found.

61.4.6 Bioaccumulation

Neely et al. (1974) have shown that bioaccumulation is related to the octanol/water partition coefficient (P) of the compound. The log octanol/water partition coefficient (log P), as calculated by the method of Hansch (Tute 1971), is 2.30, indicating that tribromomethane is somewhat lipophilic and that its bioaccumulation in organisms is possible. No laboratory or field information was found, however, to verify the potential bioaccumulation of tribromomethane.

61.4.7 Biotransformation and Biodegradation

No information pertaining specifically to the biodegradation of tribromomethane was found. In the sea many species of brown seaweed, molluscs, sponges, and bacteria metabolize halogens (Anonymous 1977). The red algae, or rhodophyta, which are known to use mostly bromine, synthesize several different halogenated organic substances. A red seaweed of the genus Asparagopsis produces tribromomethane at a concentration of 1% of the total plant composition on a dry weight basis. Since tribromomethane occurs naturally in seaweed, it is possible that some species of microorganisms could metabolize tribromomethane specifically.

61.4.8 Other Reactions

Thus far it has not been demonstrated whether mixed bromochloroforms and bromoforms arise as a result of the haloform reaction. Nonetheless, bromide, even at very low concentrations (as low as 0.1 mg/l), greatly influences chlorination reactions (Rook 1974; Morris 1975). Bromide is very rapidly oxidized to hypobromous acid by aqueous chlorine. The resulting HOBr reacts more rapidly and completely with organic matter than does HOCl (Morris 1975; Rook 1974). The bromide regenerated in the reduction of HOBr is readily reoxidized by excess HOCl and can thus serve as a catalyst in oxidation reactions (Morris 1975; Rook 1974).

Rook (1977) has suggested that tribromomethane (bromoform), which has been found in finished drinking water, may be present in such chlorinated water due to the haloform reaction. Stated simply, the haloform reaction is an aqueous chlorination reaction which occurs generally in alkaline solution with organic compounds containing the acetyl group or with structures that may be readily oxidized to the acetyl group. In the reaction, the hydrogens on the methyl component of the acetyl group are successively replaced by chlorine or other halogen and then the carbon bond to the carbonyl group is split via hydrolysis to produce a haloform and a carboxylic acid (Morris 1975). The simplified reaction is given below:

$$CH_3COR + 3HOCl \longrightarrow CCl_3COR + 3H_2O \qquad (1)$$
$$CCl_3COR + H_2O \longrightarrow CHCl_3 + RCOOH \qquad (2)$$

It is suggested that organic compounds having a structure equivalent to an acetyl group are present in the form of humic materials (specifically, fulvic acids) which cause the yellow to brown stain of surface waters (Rook 1974; Rook 1977; Morris 1975). Specifically, the carbon between two meta-positioned OH-groups of a hydroxylated aromatic ring is proposed as the most reactive site for haloform formation (Rook 1977).

61.5 Data Summary

Table 61-1 summarizes the aquatic fate data discussed above. The half-life for oxidation is a photooxidation half-life and is based on the rate of reaction of tribromomethane with hydroxyl radicals in the troposphere. The available data are insufficient to indicate the aquatic fate of tribromomethane.

Table 61-1

Summary of Aquatic Fate of Tribromomethane

Environmental Process[a]	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	No information.	-	-	Low
Oxidation	No information on aqueous oxidation; tropospheric photooxidation is relatively rapid.	-	1-2 months	Medium
Hydrolysis	Too slow to be significant.	$3.2\times10^{-11}sec^{-1}$	686 years[b]	Medium
Volatilization	No specific information; may serve as a significant transport process.	-	-	Low
Sorption	No information found.	-	-	Low
Bioaccumulation	According to the log P value calculated, bioaccumulation in organisms may be possible.	-	-	Low
Biotransformation/ Biodegradation	No specific information; in the sea, many invertebrates metabolize halogens.	-	-	Low

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. Reported as a maximum hydrolytic half-life.

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62. DICHLORODIFLUOROMETHANE

62.1 Statement of Probable Fate

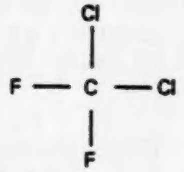
Dichlorodifluoromethane introduced into aqueous systems will most likely volatilize to the atmosphere. Once in the troposphere, dichlorodifluoromethane remains stable. It eventually diffuses into the stratosphere or is carried back to the earth during the precipitation process. Once in the stratosphere dichlorodifluoromethane is photolyzed by shorter wavelength, higher energy ultraviolet light with the subsequent formation of chlorine atoms.

Based on the information found it appears that oxidation is not an important fate process for dichlorodifluoromethane in the aquatic environment. No evidence was found for significant adsorption, bioaccumulation, hydrolysis, or biodegradation.

62.2 Identification

Dichlorodifluoromethane has been detected in surface snow in Alaska (Su and Goldberg 1976) and in the atmosphere (Singh *et al*. 1978; Lillian *et al*. 1975; Cox *et al*. 1976; Hanst 1978; Environmental Protection Agency 1975; National Research Council 1976; Howard *et al*. 1975; Howard and Durkin 1973; Su and Goldberg 1976).

The chemical structure of dichlorodifluoromethane is shown below.



Dichlorodifluoromethane

Alternate Names

Fluorocarbon-12
Freon-12

CAS NO. 75-71-8
TSL NO. PA 82000

62.3 Physical Properties

The general physical properties of dichlorodifluoromethane are as follows.

Molecular weight (Weast 1977)	129.91

Melting point (Weast 1977)	-158°C
Boiling point at 760 torr (Weast 1977)	-29.8°C
Vapor pressure at 20°C (Pearson and McConnell 1975)	4306 torr
Solubility in water at 25°C (Pearson and McConnell 1975)	280 mg/l
Log octanol/water partition coefficient (Hansch *et al*. 1975)	2.16

62.4 Summary of Fate Data

62.4.1 Photolysis

No information was found pertaining specifically to the rate of photolysis of dichlorodifluoromethane in the aquatic environment under ambient conditions.

Due to the high vapor pressure of dichlorodifluoromethane, volatilization to the atmosphere is quite rapid. The compound is tropospherically stable (Environmental Protection Agency 1975; Hanst 1975; Howard and Durkin 1973); it does not react readily with hydroxyl radicals, nor does it photodissociate in the tropsphere since it exhibits no absorption of light greater than 200 nm (Hanst 1978; Howard *et al*. 1975). Lovelock *et al*. (1973) have suggested a tropospheric residence time of 30 years for dichlorodifluoromethane before diffusion to the stratosphere.

In the stratosphere, dichlorodifluoromethane is broken down by the absorption of higher energy, shorter wavelength ultraviolet light (Hanst 1978; Rebbert and Ausloos 1975; Jayanty *et al*. 1975). The initial step in photodissociation is the abstraction of a chlorine atom (Environmental Protection Agency 1975): $CCl_2F_2 \xrightarrow{h\nu} CClF_2 + Cl\cdot$. Eventually, the photodissociation proceeds as follows:

$$CF_2Cl_2 \xrightarrow{h\nu} \cdot CF_2Cl + Cl\cdot \xrightarrow{h\nu} :CF_2 + Cl_2 \xrightarrow{h\nu} :CF_2 + 2Cl\cdot$$

Thus, according to Rebbert and Ausloos (1975) the photodissociation of dichlorodifluoromethane results in the release of two chlorine atoms since less energy is required for the cleavage of the C-Cl bond than for the cleavage of the C-F bond. According to Jayanty *et al*. (1975), the photolysis of dichlorodifluoromethane in the presence of O_2 at 213.9 nm and 25°C leads to the production of CF_2O and Cl_2 and, potentially, chlorine atoms. Chlorine atoms, released by reactions such as these, are theorized to be catalysts in the destruction of the stratospheric ozone layer (Hanst 1978; Environmental Protection Agency 1975).

62.4.2 Oxidation

No information was found pertaining to the oxidation of dichlorodifluoromethane in the aquatic environment under ambient conditons. In addition, dichlorodifluoromethane is known to be relatively stable with respect to attack by hydroxyl radicals present in the troposphere (Environmental Protection Agency 1975; Hanst 1978; Lillian et al. 1975; Cox et al. 1976; Howard et al. 1975; Howard and Durkin 1973). For instance, the bimolecular rate of reaction for dichlorodifluoromethane with hydroxyl radicals is less than $1 \times 10^{-16} cm^3 sec^{-1}$ with a corresponding lifetime (time for reduction to 1/e of the original concentration) of greater than 330 years (Cox et al. 1976). According to Howard et al. (1975), fluorocarbon compounds are highly resistant to attack by conventional oxidizing agents at temperatures below 200°C.

Assuming a troposphere-to-stratosphere turnover time (time for all but 1/e of tropospheric air to diffuse into the stratosphere) of 30 years, a tropospheric lifetime of 30 years would result in over 90 percent of tropospheric dichloridifluoromethane eventually reaching the stratosphere. Jesson et al. (1977) and Sze and Wu (1976) have postulated a shorter tropospheric lifetime, on the order of 20 years, based on analysis of the data of other workers in the field, but no known destructive mechanisms in the troposphere (sinks) are identified as being capable of removing dichlorodifluoromethane. A tropospheric lifetime of 20 years would indicate that about 40 percent of tropospheric dichlorodifluoromethane would reach the stratosphere.

62.4.3 Hydrolysis

The fluorocarbons as a group exhibit a low rate of hydrolysis in comparison to other halogenated compounds, and the rates of hydrolysis are greatly affected by temperature, pressure, and the presence of catalytic materials such as metals (Howard et al. 1975). The rate of hydrolysis of dichlorodifluoromethane at 1 atmosphere of pressure and 30°C was reported to be not discernable by the analytical technique used in the work cited (Howard et al. 1975), although the compound is known to hydrolyze under more severe conditions such as high pressure, high temperature, presence of high concentrations of metals, or any combination of these (Howard et al. 1975; Hagen and Elphingstone 1974). On the basis that conditions in the aquatic environment typically would more nearly correspond to pure water than to the more severe hydrolytic conditions mentioned above, it is postulated that hydrolysis of dichlorodifluoromethane, if it occurs, would proceed at a negligible rate in comparison to the rate of volatilization and subsequent photodissociation.

62.4.4 Volatilization

The high vapor pressure and low aqueous solubility of dichlorodifluoromethane are conducive to rapid volatilization from an aquatic environment. Although no specific data were found, volatilization is thought to be the major transport process for dichlorodifluoromethane from aqueous systems.

62.4.5 Sorption

No information was found pertaining to the adsorption of dichlorodifluoromethane onto sediments. Although the high vapor pressure indicates that volatilization is the major transport process for dichlorodifluoromethane in the aquatic environment, the log octanol/water partition coefficient (log P) of 2.16 for this compound (Hansch et al. 1975) indicates that adsorption onto organic particulates may be possible. In brief, data are inconclusive as to whether or not dichlorodifluoromethane significantly adsorbs onto sediments.

62.4.6 Bioaccumulation

Relatively little information was found pertaining specifically to the bioaccumulation of dichlorodifluoromethane. Neely *et al*. (1974) have shown that bioaccumulation is directly related to the octanol/water partition coefficient (P) of the compound. The experimentally determined log octanol/water partition coefficient (log P) of dichlorodifluoromethane is reported to be 2.16 (Hansch *et al*. 1975) indicating that dichlorodifluoromethane is lipophilic and that bioaccumulation in organisms may be possible under conditions of constant exposure. Evidence that dichlorodifluoromethane does not significantly bioaccumulate in organisms was given by Howard *et al*. (1975). The fact that dichlorodifluoromethane has a high vapor pressure (4306 mm Hg at 20°C), and consequently is very volatile, seems to exclude persistence in the aquatic environment.

62.4.7 Biotransformation and Biodegradation

No information was found pertaining to the biodegradability of dichlorodifluoromethane. According to Howard *et al*. (1975) the volatility of dichlorodifluoromethane, as well as other fluorocarbons, would limit, if not preclude, biodegradation. Su and Goldberg (1976), however, report that dichlorodifluoromethane, as well as other synthetic organic compounds, is persistent in natural waters.

62.5 Data Summary

Table 62-1 summarizes the aquatic fate discussed above. Oxidation rates are photooxidation rates and refer to the rate at which dichlorodifluoromethane is attacked by hydroxyl radicals in the troposphere. Dichlorodifluoromethane is rapidly volatilized, and its predominant fate is photolysis in the atmosphere. Once in the troposphere, dichlorodifluoromethane remains stable as a result of its extremely slow rate of reaction with hydroxyl radicals, so that much of the compound in the troposphere eventually diffuses upward to the stratosphere or is carried back to the earth during the precipitation process. Once in the stratosphere, dichlorodifluoromethane is photolyzed by shorter wavelength, higher energy ultraviolet light.

Table 62-1

Summary of Aquatic Fate of Dichlorodifluoromethane

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis [a]	Probably not significant in aquatic systems; photodissociation in the stratosphere is the primary fate of this compound.	—	30 years[b]	High
Oxidation	Not a significant fate process for this compound in the aquatic environment or the atmosphere.	$1 \times 10^{-16} cm^3 sec^{-1}$	330 years[c]	High
Hydrolysis	Is too slow to be a significant fate process.	<5mg/liter/year[d]	—	Low
Volatilization	The primary transport process from the aquatic environment.	—	—	Medium
Sorption	Data are inconclusive.	—	—	-
Bioaccumulation	Data are inconclusive.	—	—	-
Biotransformation/ Biodegradation	Volatility probably precludes biodegradation.	—	—	Low

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a. The predominant environmental process which is thought to determine the fate of the compound.

b. Reported as a stratospheric lifetime (reduction to 1/e of original concentration) of 30 years.

c. Reported as a lifetime (reduction to 1/e) greater than 330 years.

d. Too slow to be accurately determined by the analytical technique used.

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63. TRICHLOROFLUOROMETHANE

63.1 Statement of Probable Fate

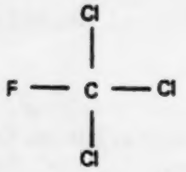
Volatilization is the major transport process for removal of trichlorofluoromethane from aquatic systems. In the troposphere, trichlorofluoromethane remains stable, but it eventually diffuses into the stratosphere or is carried back to the earth during the precipitation process. Once in the stratosphere, trichlorofluoromethane probably reacts with shorter wavelength, higher energy ultraviolet light to produce chlorine atoms. These chlorine atoms are theorized to be catalysts in the destruction of the stratospheric ozone layer.

Based on the information reviewed it does not appear that oxidation is an important fate process of trichlorofluoromethane in the aquatic environment. Evidence for adsorption, bioaccumulation, hydrolysis, and biodegradation is inconclusive.

63.2 Identification

Trichlorofluoromethane has been detected in surface waters (Su and Goldberg 1976), in surface snow in Alaska (Su and Goldberg 1976), in seawater (Lovelock _et al_. 1973), and in the atmosphere (Singh _et al_. 1978; Lillian _et al_. 1975; Cox _et al_. 1976; Hanst 1978; Environmental Protection Agency 1975; National Research Council 1976; Lovelock 1971; Howard _et al_. 1975; Howard and Durkin 1973; Lovelock 1975; Su and Goldberg 1976).

The chemical structure of trichlorofluoromethane is shown below.



Trichlorofluoromethane

CAS NO. 75-69-4
TSL NO. PB 61250

Alternate Names

Fluorocarbon-11
Freon-11

63.3 Physical Properties

The general physical properties of trichlorofluoromethane are as follows.

Molecular weight (Verschueren 1977)	137.4
Melting point (Verschueren 1977)	-111°C
Boiling point at 760 torr (Verschueren 1977)	23.8°C
Vapor pressure at 20°C (Pearson and McConnell 1975)	667.4 torr
Solubility in water	1,100 mg/l*
Log octanol/water partition coefficient (Hansch et al. 1975)	2.53

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*More than one value for the solubility of trichlorofluoromethane in water were found in the literature. The values are reported to be 1,100 mg/l at 20°C (Pearson and McConnell 1975) and 1,100 mg/l at 25°C (Verschueren 1977).

63.4 Summary of Fate Data

63.4.1 Photolysis

No information was found pertaining to the rate of photolysis of trichlorofluoromethane in the aquatic environment.

Due to the high vapor pressure of trichlorofluoromethane, volatilization to the atmosphere is quite rapid. Since trichloroflurομethane has been found in rainwater (Su and Goldberg 1976), it seems likely that some trichlorofluoromethane is washed out of the troposphere onto the earth during the precipitation process. Trichlorofluoromethane is reported to be tropospherically stable (Environmental Protection Agency 1975; Hanst 1978; Lillian et al. 1975; Cox et al. 1976; Howard et al. 1975; Howard and Durkin 1973) and does not react readily with hydroxyl radicals present in the troposphere. Lovelock et al. (1973) have suggested a residence time of 10 years, assuming no significant tropospheric degradation and complete destruction in the stratosphere. Trichlorofluoromethane does not photodissociate in the troposphere since it does not significantly absorb wavelengths of light greater than 200 nm (Hanst 1978; Howard et al. 1975).

The tropospherically stable trichlorofluoromethane eventually diffuses into the stratosphere (Hanst 1978; National Research Council 1976) where it is broken down by the attack of higher energy, shorter wavelength ultraviolet light (Hanst 1978; Environmental Protection Agency 1975; Rebbert and Ausloos 1975; Jayanty et al. 1975). Lillian *et al.* (1975) estimate a minimum stratospheric half-life for trichlorofluoromethane of 69 hours. The initial step in the photodissociation of trichlorofluoromethane is the abstraction of a chlorine atom (Environmental Protection Agency 1975): $CCl_3F \xrightarrow{h\nu} \cdot CCl_2F + Cl\cdot$ Eventually, the photodissociation proceeds as follows:

$$CFCl_3 \xrightarrow{h\nu} \cdot CFCl_2 + Cl\cdot \xrightarrow{h\nu} :CFCl + Cl_2$$

$$Cl_2 \xrightarrow{h\nu} 2Cl\cdot$$

Thus, according to Rebbert and Ausloos (1975) the photodissociation of trichlorofluoromethane results in the release of two chlorine atoms since less energy is required for the cleavage of the C-Cl bond than for the cleavage of the C-F bond. According to Jayanty *et al.* (1975) the photolysis of trichlorofluoromethane in the presence of O_2 at 213.9 nm and 25°C leads to the production of CFClO and, potentially, chlorine molecules (Cl_2). Chlorine atoms, released by reactions such as these, are theorized to be catalysts in the destruction of the stratospheric ozone layer (Hanst 1978; Environmental Protection Agency 1975).

63.4.2 Oxidation

No information was found pertaining to the oxidation of trichlorofluoromethane in the aquatic environment under ambient conditions. Trichlorofluoromethane does not react significantly with hydroxyl radicals present in the troposphere (Environmental Protection Agency 1975; Hanst 1978; Lillian *et al.* 1975; Cox *et al.* 1976; Howard *et al.* 1975; Howard and Durkin 1973) and,as a result, is tropospherically stable. For instance, the bimolecular rate of reaction for trichlorofluoromethane with hydroxyl radicals is reported to be less than $1.0 \times 10^{-17} cm^3 s^{-1}$ which corresponds to a reported tropospheric lifetime (time for reduction to 1/e of the original concentration) of much greater than 1000 years (Cox *et al.* 1976). According to Howard *et al.* (1975), fluorocarbon compounds are highly resistant to attack by conventional oxidizing agents at temperatures below 200°C.

In contrast, Jesson *et al.* (1977) interpret the available data as indicating a tropospheric lifetime for trichlorofluoromethane of 15 to 20 years, although no mechanism of tropospheric destruction (sink) is identified. Sze and Wu (1976) state that this shorter tropospheric lifetime cannot be ruled out. Assuming a tropospheric-to-stratospheric turnover time (time for all but 1/e of the tropospheric air to diffuse into the stratosphere) of 30 years, the shorter lifetime corresponds to about 40 percent of tropospheric trichlorofluoromethane reaching the stratosphere, in comparison to over 95 percent for a tropospheric lifetime of 1000 years.

63.4.3 Hydrolysis

No specific information was found indicating that trichlorofluoromethane hydrolyzes sufficiently rapidly under ambient conditions for this process to be an important environmental fate of the compound. The fluorocarbons as a group exhibit a low rate of hydrolysis in comparison to other halogenated compounds (Howard et al. 1975). The rate of hydrolysis is greatly affected by temperature, pressure, and the presence of other materials, such as high concentrations of metals which act as catalysts. In pure water, the rate of hydrolysis of trichlorofluoromethane at atmospheric pressure and 30°C is reported to be not discernable by the analytical method used in the work cited (Howard et al. 1975). Trichlorofluoromethane hydrolyzes more rapidly under conditions of high pressure, high temperature, presence of catalysts, or any combination of these (Howard et al. 1975; Hagen and Elphingstone 1974). In summary, trichlorofluoromethane would be expected to undergo hydrolysis under ambient conditions at a rate of volatilization and subsequent photodissociation.

63.4.4 Volatilization

The high vapor pressure (667.4 torr at 20°C), low solubility (1,100 mg/l reported at 20 and 25°C) and low boiling point (23.8°C at 760 torr) of trichlorofluoromethane are conducive to rapid volatilization from an aquatic environment. Though no specific data were found, volatilization is thought to be the major transport process for removal of trichlorofluoromethane from aqueous systems.

63.4.5 Sorption

No information was found pertaining to the adsorption of trichlorofluoromethane onto sediments. Although volatilization is believed to be the major transport process for this compound, the octanol/water partition coefficient (log P=2.53) of trichlorofluoromethane indicates that adsorption onto sediments may be possible. In brief, data are inconclusive as to whether or not trichlorofluoromethane significantly adsorbs onto sediments.

63.4.6 Bioaccumulation

Relatively little information was found pertaining specifically to the bioaccumulation of trichlorofluoromethane. Dickson and Riley (1976) have found trichlorofluoromethane at levels of 0.1 to 5.0 ppb, (dry weight basis) in various organs of fish and molluscs. These levels, however, do not necessarily indicate a potential for bioaccumulation.

Neely et al. (1974) have theorized that bioaccumulation is directly related to the octanol/water partition coefficient (P) of the compound. The experimentally determined log octanol/water partition coefficient (log P) of trichlorofluoromethane is reported to be 2.53 (Hansch et al. 1975), indicating that trichlorofluoromethane is lipophilic and may possibly bioaccumulate in organisms.

Howard et al. (1975) suggest that the high volatility of trichlorofluoromethane (vapor pressure 667.4 torr at 20°C) seems to make persistence in the aquatic environment unlikely.

63.4.7 Biotransformation and Biodegradation

No information was found pertaining to the biodegradability of trichlorofluoromethane. According to Howard et al. (1975) the rapid rate of volatilization expected for trichloromethane, as well as other fluorocarbons, would limit, if not preclude, biodegradation.

63.5 Data Summary

Table 63-1 summarizes the aquatic fate discussed above. The oxidation rate presented is a photooxidation rate and refers to the rate at which trichlorofluoromethane is attacked by hydroxyl radicals in the troposphere.

The primary fate of trichlorofluoromethane is photodissociation in the stratosphere, a direct result of the rapid volatilization of this compound into the atmosphere. Once in the troposphere, trichlorofluoromethane remains stable and eventually diffuses upward to the stratosphere or is carried back to earth during the precipitation process. Once in the stratosphere, trichlorofluoromethane reacts with shorter wavelength, higher energy ultraviolet light to eventually form chlorine atoms which are theorized to serve as a catalyst in destruction of the stratospheric ozone layer.

Table 63-1

Summary of Aquatic Fate of Trichlorofluoromethane

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis[a]	Probably not significant in aquatic systems; photodissociation in the stratosphere is the primary fate of this compound.	-	10 years[b]	Medium
Oxidation	Not a significant fate process for this compound.	$<1 \times 10^{-17} cm^3 sec^{-1}$	>>1000 years[c]	Medium
Hydrolysis	Is too slow to be a significant fate process.	<5mg/liter/year[d]	-	Low
Volatilization	The primary transport process from the aquatic environment.	-	-	Medium
Sorption	Inconclusive data.	-	-	-
Bioaccumulation	Evidence is inconclusive	-	-	-
Biotransformation/ Biodegradation	Volatility probably precludes biodegradation.	-	-	Low

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a. The predominant environmental process which is thought to determine the fate of the compound.

b. Reported as a stratospheric lifetime of 10 years.

c. Reported as a lifetime of much greater than 1000 years.

d. Too slow to be accurately determined by the analytical technique used.

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SECTION VI: HALOGENATED ETHERS

Chapters 64-70

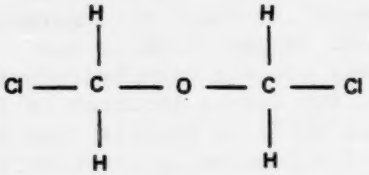
64. BIS(CHLOROMETHYL)ETHER

64.1 Statement of Probable Fate

Bis(chloromethyl)ether (BCME) hydrolyzes very rapidly (half-life 10-40 seconds) on contact with water. Although BCME also may be volatilized or oxidized, these processes proceed at a much slower rate, and are thus not competitive with hydrolysis. Hydrolytic half-lives of BCME in organisms are probably comparably short thus precluding the existence of food chain transfers.

64.2 Identification

The chemical structure of bis(chloromethyl)ether is shown below.



Bis(chloromethyl)ether

CAS NO. 542-88-1
TSL NO. KN 15750

Alternate Names

BCME
Bis-CME
sym-Dichloromethyl ether
Oxybis(chloromethane)

64.3 Physical Properties

The general physical properties of bis(chloromethyl)ether are given below.

Molecular weight (Weast 1977)	114.96
Melting point (Weast 1977)	-41.5°C
Boiling point at 760 torr (Weast 1977)	104°C
Vapor pressure at 22°C (Dreisbach 1952)	30 torr
Solubility in water at 25°C (Calc. by method of Moriguchi 1975 using the data of Quayle 1953)	22,000 mg/l
Log octanol/water partition coefficient (Calc. by Radding *et al.* 1977)	-0.38

64.4 Summary of Fate Data

64.4.1 Photolysis

Direct photolysis would not be expected to occur in surface waters or the troposphere since bis(chloromethyl)ether does not possess any chromophores that absorb radiation in the visible or near ultraviolet regions of the electromagnetic spectrum (Jaffé and Orchin 1962). No information was found that would suggest photolysis as an environmental fate process.

64.4.2 Oxidation

Radding et al. (1977) have calculated a rate constant of $<10^{-10}$ l. mole^{-1} sec^{-1}, corresponding to a half-life of >230 hours, for the reaction of hydroxyl radical with bis(chloromethyl)ether. Although oxidation is a mechanism by which BCME can be degraded, it obviously is not kinetically competitive with hydrolysis in aqueous systems. No information pertaining to the reaction of BCME with molecular oxygen in water was found. In the atmosphere, however, oxidation may compete with hydrolysis as a mechanism for BCME degradation at low humidity levels inasmuch as Tou and Kallos (1976) have reported a hydrolytic half-life of greater than 20 hours in moist air. The estimated half-life for oxidation by atmospheric hydroxyl radical is less than one day; and for oxidation by either ozone or alkylperoxyl radical, it is more than one year (Radding et al. 1977).

64.4.3 Hydrolysis

Tou et al. (1974), by careful measurements with 1 ppm BCME dissolved in water, showed that BCME hydrolyzes in circumneutral water independently of pH, and that the rate constant at 20°C is 0.018 sec^{-1}, corresponding to a half-life of approximately 38 seconds. Several other investigations corroborate this value (Van Duuren et al. 1972; Nichols and Merritt 1973; Tou and Kallos 1974; Alvarez and Rosen 1976; Tou and Kallos 1976). BCME can be formed by a reverse reaction between aqueous formaldehyde and HCl (Frankel et al. 1974). The yield after 12-24 hours is given by the empirical expression:

$$(\mathrm{BCME}) = K(\mathrm{CH_2O})(\mathrm{HCl})$$

where K is between 1.3×10^{-7} and 7×10^{-8} for concentrations of formaldehyde from 100 to 4000 ppm and HCl from 100 to 40,000 ppm at 40% relative humidity and 26°C. It should be noted that these concentrations of formaldehyde and HCl are unlikely to be encountered in environmental surface waters.

64.4.4 Volatilization

The rate of hydrolysis of bis(chloromethyl)ether is extremely rapid when the material is dissolved in water or a mixture of an organic solvent and water. Any bis(chloromethyl)ether in an industrially generated waste stream apparently would never reach the natural environment if the stream contained water. Presumably, BCME could volatilize rapidly from an aquatic system only if it were discharged in a water-immiscible solvent with a high vapor pressure.

64.4.5 Sorption

There is little information on the adsorption of BCME onto particulates. Radding *et al.* (1977) report a calculated log octanol/water partition coefficient (log P) value of -0.38 for bis(chloromethyl)ether. On the basis of this value it is suggested that very little adsorption is indicated for BCME on humus. No conclusion can be drawn about adsorption on clay or other minerals.

64.4.6 Bioaccumulation, Biotransformation and Biodegradation

No information on bioaccumulation or biodegradation has been found in the reviewed literature. BCME is much too toxic and hydrolytically unstable to permit such observations.

64.5 Data Summary

Table 64-1 summarizes the aquatic fate data discussed above for bis-(chloromethyl)ether. The aquatic fate is very rapid hydrolysis. Oxidation by photolytically produced hydroxyl radical becomes a competing process only in the atmosphere.

Table 64-1

Summary of Aquatic Fate of Bis(chloromethyl)ether

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Probably does not occur.	-	-	Medium
Oxidation	Might oxidize rapidly if released into the atmosphere.	-	>230 hours[a]	Low
Hydrolysis[b]	Rapidly hydrolyzed.	0.018 sec^{-1}	38 sec[c]	High
Volatilization	Probably not a competing process.	-	-	Medium
Sorption	Does not appear to be important.	-	-	Medium
Bioaccumulation	Probably not bioaccumulated.	-	-	High
Biotransformation/ Biodegradation	Not likely to be a competing process.	-	-	Medium

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a. This half-life for atmospheric oxidation by hydroxyl radical was calculated by Radding et al. (1977).

b. The predominant environmental process which is thought to determine the fate of the compound.

c. This half-life was reported by Tou et al. (1974).

64.6 Literature Cited

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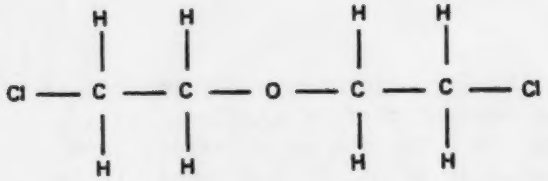
65. BIS(2-CHLOROETHYL)ETHER

65.1 Statement of Probable Fate

Based on available information, it is not possible to determine the most probable aquatic fate of bis(2-chloroethyl)ether. The relative importance of volatilization in comparison to other processes is not known for this compound. In the event that a portion of bis(2-chloroethyl)ether should enter the atmosphere, it will probably undergo photodestruction in the troposphere. Slow hydrolysis of the carbon-chlorine bonds may provide the greatest contribution to the aquatic fate of this pollutant. No information was found from which any conclusion regarding biodegradation in surface waters can be drawn.

65.2 Identification

Bis(2-chloroethyl)ether has been detected in raw and finished drinking water, and industrial effluents (Shackelford and Keith 1976). The chemical structure of bis(2-chloroethyl)ether is shown below.



$$\mathrm{Cl-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-O-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-Cl}$$

Alternate Names

1,1'-Oxybis(2-chloroethane)
Bis(β-chloroethyl)ether
Chlorex
1-Chloro-2-(β-chloroethoxy)-ethane

Bis(2-chloroethyl)ether

CAS No. 111-44-4
TSL No. KN 08750

65.3 Physical Properties

The general physical properties of bis(2-chloroethyl)ether are as follows.

Molecular weight (Weast 1977)	143.02
Melting point (Weast 1977)	-46.8°C
Boiling point at 760 torr (Weast 1977)	178°C

Vapor pressure at 20°C (Verschueren 1977)	0.71 torr
Solubility in water* (Verschueren 1977)	10,200 mg/l
Log octanol/water partition coefficient (Calc. by Leo *et al*. 1971)	1.58

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[*] Experimental data generated at room temperature; no specific temperature reported.

65.4 Summary of Fate Data

65.4.1 Photolysis

Direct photolysis would not be expected to occur in surface waters or the troposphere since bis(2-chloroethyl)ether does not possess any chromophores that absorb radiation in the visible or near ultraviolet regions of the electromagnetic spectrum (Jaffé and Orchin 1962). No information was found that would suggest photolysis as an environmental fate process.

65.4.2 Oxidation

Although water may have an inhibitory effect on the formation of ether peroxides, it apparently does not prevent their formation (Patai 1967). Since no information discussing the formation of peroxides from ethers and molecular oxygen in dilute aqueous solutions was found, it is uncertain whether ether peroxides form in the aquatic environment. Indirect photolysis, involving abstraction of alkyl hydrogens by the hydroxyl radicals normally present in surface waters, is considered to be too slow to be environmentally relevant (Dorfman and Adams 1973).

The relative importance of volatilization in comparison to other processes is unknown for this compound. In the event that a portion of bis(2-chloroethyl)ether should enter the atmosphere, it will probably undergo photodestruction in the troposphere. From the smog chamber studies of Altshuller *et al*. (1962) and Laity *et al*. (1973), it can be inferred that the half-life with respect to photodestruction in a smog chamber for ethyl ether should be four hours. Since oxidation reactions of alkyl ethers involve carbon-hydrogen scission at the carbon atom adjacent to the ether linkage, it can be expected that bis(2-chloroethyl)ether will also have a half-life of about four hours under similar conditions. It must be emphasized, however, that half-lives based on smog chamber data, do not take into account all of the meteorological variables encountered in a natural environmental airshed.

65.4.3 Hydrolysis

A reaction medium of concentrated mineral acid is usually required for the solvolysis of dialkyl ethers to proceed at a measurable rate (Fieser and Fieser 1956). Hydrolytic cleavage of dialkyl ethers is thus environmentally irrelevant. The only other covalent bonds that are capable of hydrolytic cleavage are the carbon-chlorine bonds. Böhme and Sell (1948) report a first order rate constant of chloride hydrolysis for bis-(2-chloroethyl)ether in aqueous dioxane at 100°C as 1.5×10^{-5} min^{-1}. No environmentally relevant kinetic data were found for the hydrolysis of this compound. Dilling et al. (1975) reported that the half-lives with respect to hydrolysis for one and two carbon chloroaliphatic compounds are six months to several years. Bis(2-chloroethyl)ether may have a similar hydrolytic half-life.

65.4.4 Volatilization

The vapor pressure of bis(2-chloroethyl)ether (0.71 torr at 20°C) suggests that it might be sufficiently volatile to be transported into the atmosphere. Using the approach of Mackay and Wolkoff (1973), Durkin et al. (1975) calculated the half-life with respect to volatilization for bis(2-chloroethyl)ether from a body of water to be 5.78 days. (It should be noted that this method of calculating evaporative half-lives is not universally accepted). In view of this haloether's solubility in water (10,200 mg/l), it appears likely that it could be precipitated from the atmosphere with rain and, in this manner, continuously recycle between surface water and atmosphere until it is destroyed. Because of its water solubility, some migration through the soil may occur.

Some information on the volatility of bis(2-chloroethyl)ether in a natural aquatic environment has been provided in an indirect way by Kleopfer and Fairless (1972). These investigators monitored the concentration of bis(2-chloroisopropyl)ether in the Ohio River 150 miles from an industrial outfall, and found that the pollutant was present at approximately the expected level calculated from the dilution factors that would obtain during river transport. (The calculated concentration of pollutant was 1.8 μg/l and the measured concentrations were within the range of 0.5 to 5.0 μg/l). This observation suggests that neither sedimentary sorption, volatilization, nor biodegradation were overtly operative during transport of this haloether over that particular 150 miles of the Ohio River. The vapor pressures at 20°C of bis(2-chloroethyl)ether and bis(2-chloroisopropyl)ether are 0.71 torr and 0.85 torr, respectively, and their solubilities are 10,200 mg/l and 1,700 mg/l, respectively. By inference, bis(2-chloroethyl)ether would be expected to be similarly transported without appreciable evaporation.

65.4.5 Sorption

With the exception of the field study of Kleopfer and Fairless (1972) on the transport of bis(2-chloroisopropyl)ether in the Ohio River, no information specifically pertaining to the relevance of sorption processes for beta-haloalkyl ethers within the aquatic environment was found. The results of this field study suggests that low molecular weight beta-haloalkyl ethers do not readily become immobilized as part of the bed sediment in a river system. The solubility of bis(2-chloroethyl)ether (10,200 mg/l) and the value of its log octanol/water partition coefficient (1.58, Leo *et al*. 1971) indicate little potential for adsorption on suspended organic matter.

65.4.6 Bioaccumulation

No information indicating that bis(2-chloroethyl)ether will bioaccumulate was found. Moreover, Metcalf and Sanborn (1975) maintain that compounds with solubilities of 50 mg/l or more generally have little potential for aquatic bioaccumulation. This statement is based on the direct dependence of aquatic partitioning processes upon relative solubilities; compounds soluble to the extent of 50 mg/l have been empirically observed to have little partitioning preference for biological systems or organic particulates.

65.4.7 Biotransformation and Biodegradation

No information was found from which any conclusion regarding biodegradation in surface waters can be reached with any degree of confidence. Ludzack and Ettinger (1963) found that significant degradation of bis(2-chloroethyl)ether, which had been added to Ohio River water supplemented with settled sewage, occurred only after a 25-30 day period of acclimation. Kleopfer and Fairless (1972) reported no degradation of bis(2-chloroisopropyl)ether five days after it had been added to Ohio River water.

65.5 Data Summary

Table 65-1 summarizes the preceding discussion. Atmospheric photooxidation contributes an indeterminate amount to the pollutant's destruction, and hydrolysis of the carbon-chlorine bonds is a slow but perhaps significant process. The uncertain relationship of volatilization to the destructive fate processes precludes a determination of the probable aquatic fate of bis(2-chloroethyl)ether.

Table 65-1

Summary of Aquatic Fate of Bis(2-chloroethyl)ether

Environmental Process[a]	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Direct photolysis is probably not important.	-	-	Medium
Oxidation	Atmospheric photooxidation contributes an indeterminate amount to the pollutant's fate.	-	~4 hours(e)[b]	Low
Hydrolysis	Hydrolysis of the carbon-chlorine bonds is a slow but perhaps significant process.	-	0.5-2 yr(e)[c]	Low
Volatilization	Relative importance to other processes is unknown.	-	5.78 days[d]	Low
Sorption	Does not appear to be a significant transport process.	-	-	Low
Bioaccumulation	No data available.	-	-	Low
Biotransformation/ Biodegradation	May be important in acclimated settling ponds.	-	-	Low

a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.
b. This half-life is inferred from the half-life estimated for ethyl ether based on the smog chamber data of Altshuller et al. (1962) and Laity et al. (1973).
c. Inferred from the data of Dilling et al. (1975) on chlorinated ethanes and propanes.
d. Calculated by Durkin et al. (1975) using the method of Mackay and Wolkoff (1973).

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Weast, R.C. 1977. CRC handbook of chemistry and physics. 58th Edition. CRC Press, Inc., Cleveland, Ohio. 2398p.

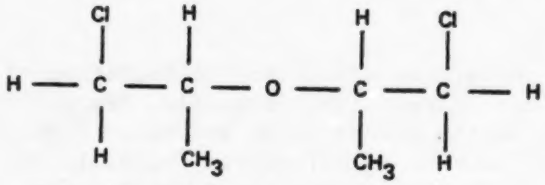
66. BIS(2-CHLOROISOPROPYL)ETHER

66.1 Statement of Probable Fate

Based on available information, it is not possible to determine the most probable aquatic fate of bis(2-chloroisopropyl)ether. The relative importance of volatilization in comparison to other processes is not known for this compound. In the event that a portion of bis(2-chloroisopropyl)-ether should enter the atmosphere, it will probably undergo photodestruction in the troposphere. Slow hydrolysis of the carbon-chlorine bonds may provide the greatest contribution to the aquatic fate of this pollutant. No information was found from which any conclusion regarding biodegradation in surface waters can be drawn.

66.2 Identification

Bis(2-chloroisopropyl)ether has been detected in finished drinking water, surface waters, industrial effluents, and sea water (Shackelford and Keith 1976). The chemical structure of bis(2-chloroisopropyl)ether is shown below.



Bis(2-chloroisopropyl)ether

CAS NO. 108-60-1
TSL NO. KN 17500

Alternate Names

Bis(2-chloro-1-methylethyl)ether
2,2'-Oxybis(1-chloropropane)
Dichlorodiisopropyl ether
2,2'-Dichloroisopropyl ether

66.3 Physical Properties

The general physical properties of bis(2-chloroisopropyl)ether are as follows.

Molecular weight (Weast 1977)	171.07
Melting point (Verschueren 1977)	-97°C
Boiling point at 760 torr (Verschueren 1977)	189°C
Vapor pressure at 20°C (Verschueren 1977)	0.85 torr

Solubility in water* (Verschueren 1977)	1,700 mg/1
Log octanol/water partition coefficient (Calc. by Leo et al. 1971)	2.58

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*Experimental data generated at room temperature; no specific temperature reported.

66.4 Summary of Fate Data

66.4.1 Photolysis

Direct photolysis would not be expected to occur in surface waters or the troposphere since bis(2-chloroisopropyl)ether does not possess any chromophores that absorb radiation in the visible or near ultraviolet regions of the electromagnetic spectrum (Jaffé and Orchin 1962). No information was found that would suggest photolysis as an environmental fate process.

66.4.2 Oxidation

Although water may have an inhibitory effect on the formation of ether peroxides, it apparently does not prevent their formation (Patai 1967). Since no information discussing the formation of peroxides from ethers and molecular oxygen in dilute aqueous solutions was found, it is uncertain whether ether peroxides form in the aquatic environment. Indirect photolysis, involving abstraction of alkyl hydrogens by the hydroxyl radicals normally present in surface waters, is considered to be too slow to be environmentally relevant (Dorfman and Adams 1973).

The relative importance of volatilization in comparison to other processes is unknown for this compound. In the event that a portion of bis(2-chloroisopropyl)ether should enter the atmosphere, it will probably undergo photodestruction in the troposphere. From the smog chamber studies of Altshuller et al. (1962) and Laity et al. (1973), it can be inferred that the half-life with respect to photodestruction in a smog chamber for ethyl ether should be four hours. Since oxidation reactions of alkyl ethers involve carbon-hydrogen scission at the carbon atom adjacent to the ether linkage, it can be inferred that bis(2-chloroisopropyl)ether will also have a half-life of about four hours under similar conditions. It must be emphasized, however, that temporal stabilities based on smog chamber data do not take into account all of the meteorological variables encountered in a natural environmental airshed.

66.4.3 Hydrolysis

A reaction medium of concentrated mineral acid is usually required for the solvolysis of dialkyl ethers to proceed at a measurable rate (Fieser and Fieser 1956). Hydrolytic cleavage of dialkyl ethers is thus environmentally irrelevant. The only other covalent bonds that are capable of hydrolytic cleavage are the carbon-chlorine bonds. Böhme and Sell (1948) report a first order rate constant of chloride hydrolysis for bis-(2-chloroethyl)ether in aqueous dioxane at 100°C as 1.5×10^{-5} min^{-1}. No environmentally relevant kinetic data were found for the hydrolysis of this compound. Dilling et al. (1975) reported that the half-lives with respect to hydrolysis for one and two carbon chloroaliphatic compounds are six months to several years. Bis(2-chloroisopropyl)ether may have a corresponding rate of hydrolysis.

66.4.4 Volatilization

The vapor pressure of bis(2-chloroisopropyl)ether (0.85 torr at 20°C) suggests that it might be sufficiently volatile to be transported into the atmosphere. Using the approach of Mackay and Wolkoff (1973), Durkin et al. (1975) calculated the half-life with respect to volatilization for bis(2-chloroisopropyl)ether from a body of water to be 1.37 days. (It should be noted that this method of calculating evaporative half-lives is not universally accepted). In view of this haloether's solubility in water (1,700 mg/l), it appears likely that it could be precipitated from the atmosphere with rain and, in this manner, continuously recycle between surface water and atmosphere until it is destroyed. Because of its water solubility, some migration through the soil may occur.

Some information on the volatility of bis(2-chloroisopropyl)ether in a natural aquatic environment has been provided by Kleopfer and Fairless (1972). These investigators monitored the concentration of bis(2-chloroisopropyl)ether in the Ohio River 150 miles from an industrial outfall, and found that the pollutant was present at approximately the expected level calculated from the dilution factors that would obtain during river transport. (The calculated concentration of pollutant was 1.8 μg/l and the measured concentrations were within the range of 0.5 to 5.0 μg/l). This observation suggests that neither sedimentary sorption, volatilization, nor biodegradation were overtly operative during transport of this haloether over that particular 150 miles of the Ohio River.

66.4.5 Sorption

With the exception of the field study of Kleopfer and Fairless (1972) on the transport of bis(2-chloroisopropyl)ether in the Ohio River, no information specifically pertaining to the relevance of sorption processes for beta-haloalkyl ethers within the aquatic environment was found. The results of this field study indicated that low molecular weight beta-haloalkyl ethers do not readily become immobilized as part of the bed sediment in a river system. The value of the log octanol/water partition coefficient of bis(2-chloroisopropyl)ether 2.58, (Leo et al. 1971) does indicate, however, some potential for adsorption on suspended organic matter.

66.4.6 Bioaccumulation

No information indicating that bis(2-chloroisopropyl)ether will bioaccumulate was found. Moreover, Metcalf and Sanborn (1975) maintain that compounds with solubilities of 50 mg/l or more generally have little potential for aquatic bioaccumulation. The basis of this statement is the strong dependence of bioaccumulation upon the partitioning processes in aquatic systems; compounds which exhibit solubility in water of 50 mg/l (or greater) have been empirically observed not to partition preferentially to biological systems or organic particulates.

66.4.7 Biotransformation and Biodegradation

No information was found from which any conclusion regarding biodegradation in surface waters can be reached with any degree of confidence. Ludzack and Ettinger (1963) found that significant degradation of bis(2-chloroethyl)ether, which had been added to Ohio River water supplemented with settled sewage, occurred only after a 25-30 day period of acclimation. Kleopfer and Fairless (1972) reported no detectable degradation of bis(2-chloroisopropyl)ether five days after it had been added to a sample of Ohio River water.

66.5 Data Summary

Table 66-1 summarizes the preceding discussion. Atmospheric photooxidation contributes an indeterminate amount to the pollutant's destruction, and hydrolysis of the carbon-chlorine bonds is a slow process. The uncertain relationship of volatilization to the destructive fate processes precludes a determination of the probable aquatic fate of bis(2-chloroisopropyl)ether.

Table 66-1

Summary of Aquatic Fate of Bis(2-chloroisopropyl)ether

Environmental Process[a]	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Direct photolysis is probably not important.	-	-	Medium
Oxidation	Atmospheric photooxidation contributes an indeterminate amount to the pollutant's fate.	-	~4 hours(e)[b]	Low
Hydrolysis	Hydrolysis of the carbon-chlorine bonds is a slow but perhaps significant process.	-	0.5-2 years[c]	Low
Volatilization	Relative importance to other processes is unknown.	-	1.37 days[d]	Low
Sorption	Does not appear to be a significant transport process.	-	-	Low
Bioaccumulation	No data available.	-	-	Low
Biotransformation/ Biodegradation	May be important in acclimated settling ponds.	-	-	Low

---

a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. This half-life is inferred from the half-life estimated for ethyl ether based on the smog chamber data of Altshuller et al. (1962) and Laity et al. (1973).

c. Inferred from the data of Dilling et al. (1975) on chlorinated ethanes and propanes.

d. Calculated by Durkin et al. (1975) using the method of Mackay and Wolkoff (1973).

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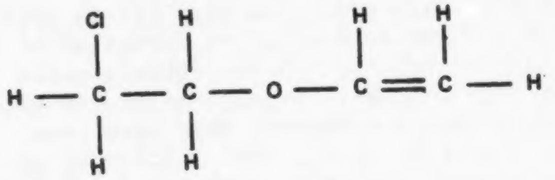
67. 2-CHLOROETHYL VINYL ETHER

67.1 Statement of Probable Fate

Based on the available information, it appears that the predominant process for removal of 2-chloroethyl vinyl ether from the aquatic environment is volatilization to the atmosphere. That portion of the pollutant which volatilizes to the troposphere is probably destroyed rapidly by photooxidation of the oxygen-substituted double bond. It should be noted, however, that the solubility of 2-chloroethyl vinyl ether is relatively high; consequently, persistence of some 2-chloroethyl vinyl ether is to be expected. Although the role of sorption onto clays and humic materials cannot be established based on the reviewed literature, such sorption processes could provide heterogeneous sites for acid-catalyzed hydrolysis. No information pertaining to biodegradation was found.

67.2 Identification

2-Chloroethyl vinyl ether has been detected in industrial effluents near Louisville, Kentucky (Shackelford and Keith 1976). The chemical structure of 2-chloroethyl vinyl ether is shown below.



2-Chloroethyl vinyl ether

CAS NO. 110-75-8
TSL NO. KN 63000

Alternate Names

(2-Chloroethoxy)-ethene
Vinyl 2-chloroethyl ether

67.3 Physical Properties

The general physical properties of 2-chloroethyl vinyl ether are as follows.

Molecular weight (Weast 1977)	106.55
Melting point	No data found
Boiling point at 760 torr (Weast 1977)	108°C

Vapor pressure at 20°C (Calc. from Dreisbach 1952)	26.75 torr
Solubility in water at 25°C (Calc. by method of Moriguchi 1975)	15,000 mg/l
Log octanol/water partition coefficient (Calc. by method of Leo *et al.* 1971)	1.28

67.4 Summary of Fate Data

67.4.1 Photolysis

2-Chloroethyl vinyl ether would not be expected to undergo direct photolysis in surface waters or the troposphere since the compound does not possess any chromophores that absorb radiation in the visible or near ultraviolet regions of the electromagnetic spectrum (Jaffé and Orchin 1962). No information was found that would suggest photolysis as an environmental fate process.

67.4.2 Oxidation

The estimated vapor pressure of 26.75 torr at 20°C (Dreisbach 1952) indicates that volatilization will be a major transport process for the removal of this compound from water. Although it is very likely that this pollutant will be reprecipitated with water during the formation of rain, its expected rate of destruction in the troposphere probably makes atmospheric photooxidation the major fate process. Organic molecules with unsaturated double bonds are the most reactive compounds that have been studied in simulated smog chambers (Altshuller *et al.* 1962; Laity *et al.* 1973). It has been extensively demonstrated that the mechanism for decomposition involves electrophilic attack by hydroxyl radical, ozone, or other oxidants on the double bond. Thus, reactivity generally increases with substitution of electron-donating groups on the two carbon atoms of the double bond. Altshuller *et al.* (1962) have reported that the half-conversion time for the disappearance of ethylene and m-xylene under the conditions employed for smog chamber studies is approximately four hours. From this value and the table of relative reactivities given by Laity *et al.* (1973), it can be inferred that the corresponding half-conversion times for ethyl ether and 2-methyl-2-butene (two extensively studied compounds) would be four hours and 30 minutes, respectively. The decomposition of 2-chloroethyl vinyl ether will undoubtedly proceed more easily than ethyl ether and may have a half-life closer to 30 minutes. It must be emphasized that the temporal stability of 2-chloroethyl vinyl ether under actual atmospheric conditions is unknown. Experiments performed in laboratory irradiation chambers are usually conducted for relatively short periods and cannot account for all of the meteorological variables within an environmental airshed.

67.4.3 Hydrolysis

The first order rate constant for the hydrolysis of 2-chloroethyl vinyl ether at 25°C and pH 7 is 4.4×10^{-10} sec^{-1} (Jones and Wood 1964). This first order rate would correspond to a maximum half-life of 0.48 years. Since this hydrolysis is second order with respect to hydrogen ion concentration and, in addition, exhibits general acid catalysis (Salomaa et al. 1966; Loudon and Ryono 1975), the hydrolytic half-life may vary considerably within the limits of the ambient aquatic environment. For example, the small amount of fully protonated phosphoric acid (H_3PO_4) still existing at neutral and slightly basic conditions can contribute a measurable catalytic effect to the hydrolysis of vinyl ethers (Loudon and Ryono 1975). Even though the log octanol/water partition coefficient is calculated as 1.28, some adsorbtion of this polar molecule can be expected by suspended clays and humic materials. Inasmuch as the cations of the clay surface are Lewis acids (Gabel and Ponnamperuma 1967), and the structure of humic materials apparently contains many phenolic acid groups (Rook 1977), general acid catalysis may occur at these sites. The extent to which heterogeneous acid catalysis could contribute to the hydrolysis of 2-chloroethyl vinyl ether is, however, unknown and must remain, at this point, purely conjectural.

67.4.4 Volatilization

Although no information pertaining specifically to the volatilization of 2-chloroethyl vinyl ether was found, the vapor pressure of 26.75 torr at 20°C, calculated from data given by Dreisbach (1952), indicates that volatilization will be important in the transport of this pollutant from the aquatic environment into the atmosphere. In view of this haloether's solubility in water (15,000 mg/l), it appears likely that it will be precipitated from the atmosphere with rain, so that a continuous cycling of this compound will occur until it is destroyed. Because of its water solubility, some migration through the soil may occur.

67.4.5 Sorption

No information specifically pertaining to sorption processes with environmental significance was found. The log octanol/water partition coefficient is calculated as 1.28 and the solubility as 15,000 mg/l indicating that there is little potential for partitioning of this aquatic pollutant into suspended lipophilic material; however, it is possible that this polar, unsaturated molecule could become transitorily sorbed by suspended clays and humic materials.

67.4.6 Bioaccumulation

No information was found indicating that 2-chloroethyl vinyl ether will bioaccumulate. Moreover, Metcalf and Sanborn (1975) maintain that compounds with solubilities of 50 mg/l or more generally have little potential for aquatic bioaccumulation. This statement is based on the empirically observed effect of aquatic partitioning processes upon bioaccumulation; compounds with solubilities of 50 mg/l (or greater) do not partition preferentially to biological systems or organic particulates.

67.4.7 Biotransformation and Biodegradation

No information was found from which any conclusion regarding biodegradation can be reached with any degree of confidence.

67.4.8 Other Reactions

Chlorination of 2-chloroethyl vinyl ether can introduce a chlorine substituent at either carbon atom that is adjacent to the ether linkage (Summers 1955). As a consequence of this reaction, 2-chloroethyl vinyl ether can be modified to an alpha-chloroether in a water treatment facility. alpha-Chloroethers are very hydrolytically unstable and usually decompose within seconds (Summers 1955; Tou and Kallos 1974).

67.5 Data Summary

Table 67-1 summarizes the aquatic fate data discussed above. The predominant transport process for removal of 2-chloroethyl vinyl ether from the aquatic environment appears to be volatilization to the atmosphere. Photooxidation in the troposphere should be very rapid, and it is probably the main fate process. Although the extent of sorption onto clays and humic materials cannot be established, such sorption processes could provide heterogeneous sites for acid-catalyzed hydrolysis.

Table 67-1

Summary of Aquatic Fate of 2-Chloroethyl vinyl ether

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Direct photolysis is probably not important.	-	-	Medium
Oxidation[a]	Atmospheric photooxidation is probably the most important degradative process.	-	~30 min(e)[b]	Medium
Hydrolysis	May be important as a minor degradative process if the compound is adsorbed by suspended clays or fulvic acids.	4.4×10^{-10} sec^{-1}[c]	~0.48 years[d]	Medium
Volatilization	Probably the main transport process, but no specific data were found.	-	-	Low
Sorption	No specific data found; may provide sites for heterogeneous acid-catalyzed hydrolysis.	-	-	Low
Bioaccumulation	No specific data found; probably not important.	-	-	Low
Biotransformation/ Biodegradation	No data found; not possible to make any assessment.	-	-	Low

a. The predominant environmental process which is thought to determine the fate of the compound.

b. This half-life is inferred from the half-life estimated for 2-methyl-2-butene from the smog chamber data of Altshuller et al. (1962) and Laity et al. (1973).

c. This is the minimum rate of hydrolysis of the vinyl ether linkage calculated for pH 7 at 25°C in pure water from the data of Jones and Wood (1964).

d. This is the maximum half-life calculated for pH 7 at 25°C in pure water.

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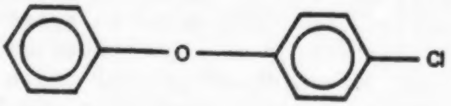
68. 4-CHLOROPHENYL PHENYL ETHER

68.1 Statement of Probable Fate

It is not possible to determine the most probable aquatic fate for 4-chlorophenyl phenyl ether from available data. This pollutant is reported to be rapidly degraded by acclimated sewage sludge, but biodegradation data from river-water die-away experiments indicate that this compound has a potential for persistence in natural surface waters. Sorption by organic-rich sediments and bioaccumulation in fish have been demonstrated. Although photolysis may make a minor contribution to the degradation of this pollutant near the air-water surface, oxidation and hydrolysis are probably not important as fate processes. The role of volatilization is uncertain.

68.2 Identification

The chemical structure of 4-chlorophenyl phenyl ether is presented below.



4-Chlorophenyl phenyl ether

CAS NO. 7005-72-3
TSL NO. None assigned

Alternate Names

1-Chloro-4-phenoxybenzene
p-Chlorophenyl phenyl ether
4-Chlorodiphenyl ether
4-Chlorophenyl ether
Monochlorodiphenyl oxide

68.3 Physical Properties

The general physical properties are as follows.

Molecular weight (Calc. from Weast 1977)	203.66
Melting point (Dow Chemical Company 1979)	-8°C*
Boiling point at 760 torr (Mailhe and Murat 1912)	284°C**

Vapor pressure at 25°C (Calc. by Branson 1977)	0.0027 torr
Solubility in water at 25°C (Branson 1977)	3.3 mg/l
Log octanol/water partition coefficient (Branson 1977)	4.08

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*Brewster and Stevenson (1940) report a melting point of 46-47°C for 2-chlorophenyl phenyl ether, and they were apparently unable to prepare a crystalline sample of 4-chlorophenyl phenyl ether.

**Dow Chemical Company (1979) has determined the boiling point at 760 torr to be 293.03°C.

68.4 Summary of Fate Data

68.4.1 Photolysis

4-Chlorophenyl phenyl ether has electromagnetic absorption maxima at 272, 279 and 293 nm (Choudhry *et al*. 1977). Irradiation of a methanolic solution in Pyrex containers ($\lambda > \underline{290 \text{ nm}}$) results only in dechlorination and the production of diphenyl ether (Choudhry *et al*. 1977). Although diphenyl ether does not absorb electromagnetic radiation above 300 nm to an appreciable extent (Ungnade 1953), there is the possibility of a photochemically induced rearrangement which yields ortho- and para-hydroxybiphenyl and a trace of phenol (Ogata *et al*. 1970). No information was found from which rates of photodegradation in the aquatic environment could be estimated.

68.4.2 Oxidation

No information was found in the reviewed literature that would support any role for oxidation of this compound as an aquatic fate. Indirect photolysis, involving interaction of hydroxyl radical with the aromatic ring, is considered to be too slow in water to be environmentally significant for this compound (Dorfman and Adams 1973).

It is at present uncertain how much of this pollutant will volatilize into the atmosphere from surface waters (see Section 68.4.4). Any 4-chlorophenyl phenyl ether that enters into the troposphere will be subject to photodegradation and reprecipitation with rain. The atmospheric half-life of unsubstituted benzene, proposed by Darnall *et al*. (1976), is 2.4 to 24 hours. According to Laity *et al*. (1973), a chlorine substituent on an aromatic ring should decrease its susceptibility to photodegradation in the troposphere. Although an oxygen substituent should facilitate destruction, it is unknown what effect the presence of both groups would have on the atmospheric destruction of 4-chlorophenyl phenyl ether.

68.4.3 Hydrolysis

No information was found in the reviewed literature that would indicate hydrolysis as an aquatic fate for this compound. It is, however, considered to be unlikely that any of the covalent bonds of 4-chlorophenyl phenyl ether will hydrolyze at ambient environmental conditions, since the negative charge-density of the aromatic ring will impede the nucleophilic attack of water or hydroxide ion.

68.4.4 Volatilization

The rate of evaporation from water of 4-chlorophenyl phenyl ether has been calculated by Branson (1977), using the equations of Liss and Slater (1974), to be 7.0 cm-hr^{-1}. The half-life, corresponding to this evaporative rate constant for a pond one meter deep, is approximately seven hours (Branson 1978). Some assumptions made in the development of these equations were: 1) the pollutant is in solution, rather than in suspended, sorbed, colloidal, or complexed form; 2) the vapor is in equilibrium with the liquid at the interface; 3) water diffusion or mixing is sufficiently rapid so that the concentration at the interface approaches that of the bulk of the water; and 4) the rate of evaporation of water is negligibly affected by the presence of solutes and suspended matter. This calculated evaporative half-life should, therefore, be considered as a minimum half-life, since it is highly probable that 4-chlorophenyl phenyl ether will be sorbed by both organic particulates and suspended clays (see Section 68.4.5).

68.4.5 Sorption

The octanol/water partition coefficient for 4-chlorophenyl phenyl ether, corresponding to log P = 4.08 (Branson 1977), is indicative of a marked preference for lipophilic organic materials over water. In addition, the polar nature of the ether bond and the carbon-halogen bond, coupled with the compound's miscibility with most lipophilic material ensures sorption of 4-chlorophenyl phenyl ether by organic detritus. Adsorption by clay particles is also thought to be highly probable, inasmuch as the polarity and planar geometry of this molecule should facilitate its intercalation within the layered clay structure. Evidence for sorption by suspended organic material is given by a sediment to water distributional ratio of 4:1 during biodegradation studies with sludge (Branson 1977).

68.4.6 Bioaccumulation

Limited information was found in the reviewed literature from which bioaccumulation could be evaluated. Several loading concentrations of 4-chlorophenyl phenyl ether in water were tested for bioconcentration inrainbow trout (Branson 1977). Trout muscle reached a steady-state after 8.9 days and exhibited a bioconcentration factor of 736 ± 89. The log octanol/water partition coefficient also indicates a definite potential for bioaccumulation in aquatic ecosystems.

68.4.7 Biotransformation and Biodegradation

Branson (1978) has reported that the half-life of 4-chlorophenyl phenyl ether with respect to biodegradation in activated sludge is approximately four hours. Data of greater relevance to natural surface waters were obtained in a river-water die-away experiment (Branson 1978). Two water samples, taken from two different locations in the Tittabawassee River and spiked with the pollutant at a concentration of 1 mg/l, showed two different rates of biodegradation. One sample exhibited no detectable degradation before 120 hours and the other, no degradation before 312 hours. Greater than 90 percent degradation required 264 hours in the first sample and 528 hours in the second. The experiments illustrated that biodegradation rate constants are not reproducible when the microbial populations have a dissimilar history. In these two experiments the half-lives with respect to biodegradation would be rather meaningless since both samples exhibited lag periods (during which loss of the pollutant was undetectable) that were approximately one-half of the time required for 90 percent degradation. Thus, it is reasonable to assume that genetic induction levels for most degradative organisms would not be reached except in the vicinity of discharges. In a non-stagnant body of surface water, a distinct microbial population would probably not be in contact with the pollutant long enough to become acclimated.

68.5 Data Summary

Table 68-1 summarizes the aquatic fate data discussed above for 4-chlorophenyl phenyl ether. Information on this compound is limited and a statement of its most probable aquatic fate is, therefore, not feasible at this time. This ether is reported to be biodegradable by acclimated sewage sludge, and there is also a possibility that photolysis might contribute to its destruction near the air-water surface. Biodegradation in most natural surface waters, however, would appear not to be an important process, whereas bioaccumulation in fish has been demonstrated and sorption by organic sediments may be important. The role of volatilization is uncertain because of a lack of scientific concensus on methods of calculating rates of pollutant volatilization from natural surface waters. Oxidation and hydrolysis are probably not important as fate processes.

Table 68-1

Summary of Aquatic Fate of 4-Chlorophenyl Phenyl Ether

Environmental Process[a]	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	A possible fate process near the air-water surface.	-	-	Low
Oxidation	Not environmentally significant.	-	-	Low
Hydrolysis	Not environmentally significant.	-	-	Low
Volatilization	Significance cannot at this time be assessed due to a lack of scientific consensus on calculating rates of evaporative loss from natural surface waters.	-	-	Low
Sorption	Adsorption may be an important transport process and also serve as a transient environmental reservoir.	-	-	Medium
Bioaccumulation	The value of the log octanol/water partition coefficient indicates a potential for bioaccumulation in aquatic ecosystems. Trout muscle exhibits a bioconcentration factor of approximately 800X.	-	-	High
Biotransformation/ Biodegradation	This pollutant is rapidly degraded by activated sewage sludge, but data from river-water die-away experiments indicate potential persistence in natural surface waters.	-	∿4 hours[b]	Medium

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. Half-life with respect to biodegradation has been measured only in activated sewage sludge (Branson 1978).

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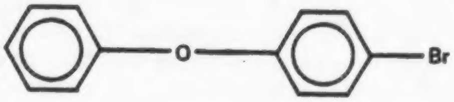
69. 4-BROMOPHENYL PHENYL ETHER

69.1 Statement of Probable Fate

Very little information pertaining to the environmental transport and fate of 4-bromophenyl phenyl ether was found, and it is, therefore, not possible to determine the most probable aquatic fate at this time. Some inferences can be drawn from experiments performed with this pollutant's chloro analog. 4-Chlorophenyl phenyl ether is reported to be rapidly degraded by acclimated sewage sludge, but biodegradation data from river-water die-away experiments indicate that this compound has a potential for persistence in natural surface waters. Sorption by organic-rich sediments and bioaccumulation in fish may be important. Although photolysis may make a minor contribution to degradation near the air-water surface, oxidation and hydrolysis are probably not important as fate processes. The role of volatilization in the removal of halogenated aromatic ethers from aquatic systems has not been demonstrated and remains uncertain.

69.2 Identification

The chemical structure of 4-bromophenyl phenyl ether is shown below.



Alternate Names

1-Bromo-4-phenoxybenzene
p-Bromophenyl phenyl ether
4-Bromodiphenyl ether
4-Bromophenyl ether

4-Bromophenyl phenyl ether

CAS NO. 101-55-3
TSL NO. None assigned

69.3 Physical Properties

The general physical properties of 4-bromophenyl phenyl ether are given below.

Molecular weight (Weast 1977)	249.11

Melting point (Weast 1977)	18.72°C
Boiling point at 760 torr (Weast 1977)	310.14°C
Vapor pressure at 20°C (Calc. from Dreisbach 1952)	0.0015 torr
Solubility in water	No data found
Log octanol/water partition coefficient (Calc. by method of Leo *et al*. 1971 using the data of Branson 1977)	4.28

69.4 Summary of Fate Data

69.4.1 Photolysis

It is reasonable to assume that 4-bromophenyl phenyl ether will absorb electromagnetic radiation in the ultraviolet region of the terrestrial solar spectrum, since its analog, 4-chlorophenyl phenyl ether, has electromagnetic absorption maxima at 272, 279 and 293 nm (Choudhry *et al*. 1977). Irradiation of a methanolic solution of 4-chlorophenyl phenyl ether in Pyrex containers ($\lambda >$ 290 nm) results only in dechlorination and the production of diphenyl ether (Choudhry *et al*. 1977). Although unsubstituted diphenyl ether apparently does not absorb electromagnetic radiation above 300 nm to an appreciable extent (Ungnade 1953), there is the possibility of a photochemically induced rearrangement which yields ortho- and para-hydroxybiphenyl and a trace of phenol (Ogata *et al*. 1970). No information was found from which rates of photodegradation in the aquatic environment could be estimated.

69.4.2 Oxidation

No information was found in the reviewed literature that would support any role for oxidation of this compound as an aquatic fate. Indirect photolysis, involving interaction of hydroxyl radical with the aromatic ring, is considered to be too slow in water to be environmentally significant for this compound (Dorfman and Adams 1973).

It is at present uncertain how much of this pollutant will volatilize into the atmosphere from surface waters (see Section 69.4.4). Any 4-bromophenyl phenyl ether that enters into the troposphere will be subject to photodegradation and reprecipitation with rain. The atmospheric half-life of unsubstituted benzene, proposed by Darnall et al. (1976), is 2.4 to 24 hours. According to Laity et al. (1973), a halogen substituent on an aromatic ring should decrease its susceptibility to photodegradation in the troposphere. Although the electron-donating resonance effect of an oxygen substituent should facilitate destruction, it is uncertain how the presence of both groups will affect the atmospheric destruction of 4-bromophenyl phenyl ether.

69.4.3 Hydrolysis

No information was found in the reviewed literature that would indicate hydrolysis as an aquatic fate for this compound. It is, however, considered to be unlikely that any of the covalent bonds of 4-bromophenyl phenyl ether will hydrolyze at ambient environmental conditions, since the negative charge-density of the aromatic ring will impede the nucleophilic attack of water or hydroxide ion.

69.4.4 Volatilization

The rate constant for evaporation from water of 4-chlorophenyl phenyl ether has been calculated by Branson (1977), using the equations of Liss and Slater (1974), to be 7.0 $cm\text{-}hr^{-1}$. The half-life, corresponding to this evaporative rate constant for a pond one meter deep, is approximately seven hours (Branson 1978). A similar calculated rate constant can be expected for the structurally analgous 4-bromophenyl phenyl ether. Some assumptions made in the development of these equations were: 1) the pollutant is in solution, rather than in suspended, sorbed, colloidal, or complexed form; 2) the vapor is in equilibrium with the liquid at the interface; 3) water diffusion or mixing is sufficiently rapid so that the concentration at the interface approaches that of the bulk of the water; and 4) the rate of evaporation of water is negligibly affected by the presence of solutes and suspended matter. This calculated evaporative half-life should, therefore, be considered as a minimum half-life, since it is highly probable that halogenated diphenyl ethers will be sorbed by both organic particulates and suspended clays (see Section 69.4.5).

69.4.5 Sorption

The octanol/water partition coefficient for 4-bromophenyl phenyl ether, corresponding to log P = 4.28 (Leo et al. 1971; Branson 1977), is indicative of a marked preference for lipophilic organic materials over water. In addition, the polar nature of the ether bond and the carbon-halogen bond, coupled with the compound's miscibility with most lipophilic material ensures sorption of 4-bromophenyl phenyl ether by organic detritus. Adsorption by clay particles is also thought to be highly probable, inasmuch as the polarity and planar geometry of this molecule should facilitate its intercalation within the layered clay structure. Evidence for sorption by suspended organic material is given by a sediment to water distributional ratio of 4:1 for 4-chlorophenyl phenyl ether during biodegradation studies with sludge (Branson 1977).

69.4.6 Bioaccumulation

Limited information was found in the reviewed literature from which bioaccumulation could be evaluated. Several loading concentrations in water of the structurally analogous pollutant, 4-chlorophenyl phenyl ether, were tested for bioconcentration in rainbow trout (Branson 1977). Trout muscle reached a steady-state after 8.9 days and exhibited a bioconcentration factor for 4-chlorophenyl phenyl ether of 736 ± 89. It can be expected that 4-bromophenyl phenyl ether will behave similarly. The log octanol/water partition coefficient also indicates a definite potential for bioaccumulation in aquatic ecosystems.

69.4.7 Biotransformation and Biodegradation

No specific information was found in the reviewed literature with which to assess the biodegradation of 4-bromophenyl phenyl ether. Since this pollutant is structurally analogous to 4-chlorophenyl phenyl ether, it may exhibit similar properties with respect to biodegradation.

Branson (1978) has reported that the biodegradative half-life of 4-chlorophenyl phenyl ether in activated sludge is approximately four hours. Data of greater relevance to natural surface waters were obtained in a river-water die-away experiment (Branson 1978). Two water samples, taken from two different locations in the Tittabawassee River and spiked with the pollutant at a concentration of 1 mg/l, showed two different rates of biodegradation. One sample exhibited no detectable degradation before 120 hours and the other, no degradation before 312 hours. Greater than 90 percent degradation required 264 hours in the first sample and 528 hours in the second. The experiments illustrated that biodegradation rate constants are not reproducible when the microbial populations have a dissimilar history. In these two experiments the half-lives with respect to biodegradation are rather meaningless since both samples exhibited lag periods (during which loss of the pollutant was undetectable) that were approximately one-half of the time required for 90 percent degradation. Thus, it is reasonable to assume that genetic induction levels for most degradative organisms will not be reached except in the vicinity of discharges. In a non-stagnant body of surface water, a distinct microbial population would probably not be in contact with the pollutant long enough to become acclimated.

69.5 Data Summary

Table 69-1 summarizes the aquatic fate data discussed above for 4-bromophenyl phenyl ether. Information on this compound is very limited and a statement of its most probable aquatic fate is, therefore, not feasible at this time. The structurally analogous pollutant, 4-chlorophenyl phenyl ether, is reported to be biodegradable by acclimated sewage sludge, and there is also a possibility that photolysis might contribute to environmental destruction near the air-water surface. Based on data obtained from experiments with 4-chlorophenyl phenyl ether, biodegradation in most natural surface waters does not appear to be an important process, whereas bioaccumulation in fish and sorption by organic sediments may be important. The role of volatilization is uncertain because of a lack of scientific concensus on methods of calculating rates of pollutant volatilization from natural surface waters. Oxidation and hydrolysis are probably not important as fate processes.

Table 69-1

Summary of Aquatic Fate of 4-Bromophenyl Phenyl Ether

Environmental Process[a]	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	A possible fate process near the air-water surface.	-	-	Low
Oxidation	Not environmentally significant.	-	-	Low
Hydrolysis	Not environmentally significant.	-	-	Low
Volatilization	Significance cannot at this time be assessed due to a lack of scientific consensus on calculating rates of evaporative loss from natural sur= face waters.	-	-	Low
Sorption	Adsorption may be an important transport process and also serve as a transient environmental reservoir.	-	-	Low
Bioaccumulation	The value of the log octanol/water partition coefficient indicates a potential for bioaccumulation in aquatic ecosystems. Trout muscle exhibits a bioconcentration factor of approximately 800X for a structurally analogous pollutant.	-	-	Low
Biotransformation/ Biodegradation	4-Chlorophenyl phenyl ether is rapidly degraded by activated sewage sludge, but data from river-water die-away experiments indicate potential persistence in natural surface waters. 4-Bromophenyl phenyl ether may behave similarly.	-	~4 hours[b]	Low

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.
b. Half-life with respect to biodegradation of 4-chlorophenyl phenyl ether in activated sewage sludge (Branson 1978).

69.6 Literature Cited

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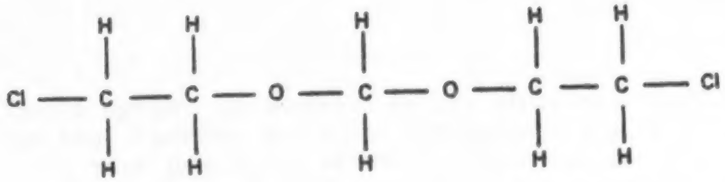
70. BIS(2-CHLOROETHOXY)METHANE

70.1 Statement of Probable Fate

Based on the available data, it appears that the most probable fate of bis(2-chloroethoxy)methane in the aquatic environment is slow hydrolysis. Neither volatilization nor sorption processes would seem to be able to affect the transport of this highly soluble, slightly volatile compound. No information pertaining to biodegradation was found.

70.2 Identification

Bis(2-chloroethoxy)methane has been detected in industrial effluents (Shackelford and Keith 1976). The chemical structure of bis(2-chloroethoxy)methane is shown below.



$$\begin{array}{ccccccccccccccccc} & & H & & H & & & & H & & & & H & & H & & \\ & & | & & | & & & & | & & & & | & & | & & \\ Cl & - & C & - & C & - & O & - & C & - & O & - & C & - & C & - & Cl \\ & & | & & | & & & & | & & & & | & & | & & \\ & & H & & H & & & & H & & & & H & & H & & \end{array}$$

Bis(2-chloroethoxy)methane

CAS NO. 111-91-1
TSL NO. PA 36750

Alternate Names
Dichlorodiethyl methylal
Bis(β-chloroethyl)formal
β,β,-Dichlorodiethyl formal

70.3 Physical Properties

General physical properties of bis(2-chloroethoxy)methane are as follows.

Molecular weight (Webb *et al.* 1962)	173.1
Melting point	No data found
Boiling point at 760 torr (Webb *et al.* 1962)	218.1°C*

Vapor pressure at 20°C (Calc. from Dreisbach 1952 based on the data of Webb *et al*. 1962)	<0.1 torr
Solubility in water at 25°C (Calc. by method of Moriguchi 1975)	81,000 mg/l
Log octanol/water partition coefficient (Calc. based on method of Leo *et al*. 1971)	1.26

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*The boiling point at 760 torr has been reported as 105°-106° by Durkin *et al*. (1975). Based on the detailed study of Webb *et al*. (1962) on the properties of this pollutant and other compounds in this series, the value reported by Durkin *et al*. (1975) is incorrect.

70.4 Summary of Fate Data

70.4.1 Photolysis

Bis(2-chloroethoxy)methane would not be expected to undergo direct photolysis in surface waters or the troposphere since the compound does not possess any chromophores that absorb radiation in the visible or near ultraviolet regions of the electromagnetic spectrum (Jaffé and Orchin 1962). No information was found that would suggest photolysis as an environmental fate process.

70.4.2 Oxidation

Even though water has an inhibitory effect on the formation of ether and acetal peroxides, it apparently does not prevent their formation (Patai 1967). Since no information discussing the efficacy of molecular oxygen in dilute aqueous solutions to form ether and acetal peroxides was found, it is uncertain whether such peroxides exist in the aquatic environment. Indirect photolysis, involving abstraction of alkyl hydrogens by the hydroxyl radicals normally present in surface waters, is considered to be too slow to be environmentally relevant (Dorfman and Adams 1973).

70.4.3 Hydrolysis

There are two sites within this molecule wherein hydrolysis could take place: (1) the carbon-oxygen bonds of the acetal linkage and (2) the carbon-chlorine bonds. The hydrolysis of acetal bonds is acid catalyzed. Kankaanperä (1969) gives this acid-catalyzed rate constant for bis(2-chloroethoxy)methane as 2.53×10^{-6} liter mole^{-1} sec^{-1}. Applying the assumptions of Radding *et al*. (1977), the maximum hydrolytic half-life in pure water at pH 7 and 25°C would be within the range of thousands of years. What effect suspended clays and humic material would have on this rate is purely conjectural.

No environmentally relevant kinetic data were found for the hydrolysis of the carbon-chlorine bond of this compound. Dilling et al. (1975) reported that the half-lives with respect to hydrolysis for one and two carbon chloroaliphatic compounds are six months to several years. Bis(2-chloroethoxy)methane may have a corresponding rate of hydrolysis.

70.4.4 Volatilization

Although no information pertaining specifically to the volatilization of bis(2-chloroethoxy)methane was found, the estimated vapor pressure of less than 0.1 torr based on the relationships given by Dreisbach (1952) and the data reported by Webb et al. (1962) indicates that volatilization would not be an important transport process. Furthermore, the calculated solubility of 81,000 mg/l and the expected hydrogen bonding between the acetal oxygen atoms and the water of solvation virtually precludes any role for volatilization as a removal mechanism from water.

70.4.5 Sorption

No information specifically pertaining to sorption processes with environmental significance was found. The log octanol/water partition coefficient, calculated as 1.26, projects little potential for adsorption by lipophilic materials, and the aqueous solubility of 81,000 mg/l indicates that whatever sorption processes occur will be only of a transitory nature. This summation, however, does not preclude a possible catalytic role in hydrolysis for suspended particulates.

70.4.6 Bioaccumulation

No information was found indicating that bis(2-chloroethoxy)-methane will bioaccumulate. Based on experimental and empirical data, Metcalf and Sanborn (1975) maintain that compounds with aqueous solubilities of about 50 mg/l or greater generally show little potential for bioaccumulation. The aqueous solubility of bis(2-chloroethoxy)methane, calculated by the method of Moriguchi (1975) to be 81,000 mg/l, appears to be much higher than the arbitrary 50 mg/l limit suggested by Metcalf and Sanborn (1975).

70.4.7 Biotransformation and Biodegradation

No information was found from which any conclusion regarding biodegradation can be reached with any degree of confidence.

70.5 Data Summary

Table 70-1 summarizes what is known about the aquatic fate of bis(2-chloroethoxy)methane. Neither volatilization nor sorption appear to affect the transport of this highly soluble, slightly volatile compound. The most probable fate for bis(2-chloroethoxy)methane is slow hydrolysis.

Table 70-1

Summary of Aquatic Fate of Bis(2-chloromethoxy)Methane

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Direct photolysis is probably not important.	-	-	Medium
Oxidation	Oxidation in the aquatic environment is irrelevantly slow.	-	-	Low
Hydrolysis [a]	This may be the only degradative process that is operative.	2.53×10^{-6} l.mole^{-1} sec^{-1} [b]	0.5-2 years [c]	Low
Volatilization	Not a viable transport process.	-	-	Medium
Sorption	Not a viable transport process.	-	-	Medium
Bioaccumulation	No specific data found; probably not important.	-	-	Low
Biotransformation/ Biodegradation	No data found; not possible to make any assessment.	-	-	Low

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a. The predominant environmental process which is thought to determine the fate of the compound.

b. This is the minimum rate constant for acid catalyzed hydrolysis of the acetal linkage at 25°C reported by Kankaanperä (1969).

c. Inferred from the data of Dilling et al. (1975) on chlorinated ethanes and propanes.

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SECTION VII: MONOCYCLIC AROMATICS

Chapters 71-93

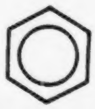
71. BENZENE

71.1 Statement of Probable Fate

Based on the information found, it appears that the predominant process for removal of benzene from the water column is volatilization to the atmosphere. That portion of the benzene which volatilizes to the atmosphere is probably depleted at a fairly rapid rate due to attack by hydroxyl radicals. It must be noted, however, that the solubility of benzene in water is relatively high; consequently, persistence of some benzene in the water column would be expected. Although the role of benzene sorption onto sediments and suspended solids cannot be established based on the reviewed literature, there is evidence of gradual biodegradation of benzene at low concentrations by aquatic microorganisms. The rate of benzene biodegradation is enhanced when other hydrocarbons are present.

71.2 Identification

Benzene has been detected in finished drinking water (U.S. Environmental Protection Agency 1975), in water and sediment samples from the lower Tennessee River in ppb concentrations (Goodley and Gordon 1976) and in the atmosphere (Howard and Durkin 1974). The chemical structure of benzene is shown below.



Benzene

CAS NO. 71-43-2
TSL NO. CY 14000

Alternate Names

Benzol
Cyclohexatriene

71.3 Physical Properties

The general physical properties of benzene are as follows.

Molecular weight (Weast 1977)	78.12
Melting point (Weast 1977)	5.5°C

Boiling point at 760 torr (Weast 1977)	80.1°C
Vapor pressure at 25°C* (Mackay and Leinonen 1975)	95.2 torr
Solubility in water	**
Log octanol/water partition coefficient	***

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*Vapor pressure values found in the literature include 45.5 torr at 10°C (Mackay and Leinonen 1975), 95.2 torr at 25°C (Mackay and Leinonen 1975; Mackay and Wolkoff 1973), and 100 torr at 26.075°C (Howard and Durkin 1974).

**Several values for the solubility of benzene in water were found in the literature. Some of the reported values found in the literature include 1750 mg/l at 10°C (Mackay and Leinonen 1975), 820 mg/l at 22°C (Chiou *et al*. 1977), 1780 mg/l at 25°C (Mackay and Wolkoff 1973; Mackay and Leinonen 1975), and 1800 mg/l at 25°C (Howard and Durkin 1974).

***The log octanol/water partition coefficient of benzene is reported to be 1.95 by Leo *et al*. (1971) and 2.13 by Chiou *et al*. (1977).

71.4 Summary of Fate Data

71.4.1 Photolysis

Since the ozone layer in the upper atmosphere effectively filters out wavelengths of light less than 290 nm, and since the ultraviolet spectrum of benzene indicates that this compound does not absorb wavelengths of light longer than 260 nm (Bryce-Smith and Gilbert 1976) direct excitation of benzene in the environment is unlikely unless a substantial wavelength shift is caused by the media (Howard and Durkin 1974). For instance, although benzene does not absorb light directly in appreciable amounts at wavelengths longer than 280 nm when dissolved in cyclohexane (Silverstein and Bassler 1968), slight shifts in wavelength absorption might be expected in more representative environmental media such as water or the surface of particulate organic matter (Howard and Durkin 1974).

71.4.2 Oxidation

No specific information pertaining to oxidation of benzene in the aqueous environment under ambient conditions was found. Howard and Durkin (1974), however, report that catalysts, elevated temperature, elevated pressure, or any of these conditions operating together may serve as initiators of benzene oxidation. Based on this information, it can be

Boiling point at 760 torr (Weast 1977)	80.1°C
Vapor pressure at 25°C* (Mackay and Leinonen 1975)	95.2 torr
Solubility in water	**
Log octanol/water partition coefficient	***

---

*Vapor pressure values found in the literature include 45.5 torr at 10°C (Mackay and Leinonen 1975), 95.2 torr at 25°C (Mackay and Leinonen 1975; Mackay and Wolkoff 1973), and 100 torr at 26.075°C (Howard and Durkin 1974).

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71.4.2 Oxidation

No specific information pertaining to oxidation of benzene in the aqueous environment under ambient conditions was found. Howard and Durkin (1974), however, report that catalysts, elevated temperature, elevated pressure, or any of these conditions operating together may serve as initiators of benzene oxidation. Based on this information, it can be inferred that direct oxidation of benzene in environmental waters is unlikely.

Inasmuch as the main transport process that would account for removal of benzene from water appears to be volatilization, the atmospheric destruction of benzene probably is much more likely than any other fate process. These complex photochemical reactions have been studied in simulated smog chambers (Altshuller *et al.* 1962; Laity *et al.* 1973) that measured the rate of disappearance of the volatilized organic material. The half-conversion time of m-xylene and 1,3,5-trimethylbenzene have been reported to be somewhat less than four hours (Altshuller *et al.* 1962). From this value and the table of relative reactivities given by Laity *et al.* (1973), it can be inferred that the corresponding range for the half-conversion time for benzene would be approximately 20 to 50 hours. This value for the estimated half-conversion time of benzene is in reasonable agreement with the estimated half-life of benzene proposed by Darnall *et al.* (1976) of 2.4 to 24 hours. This half-life value is based on the assumptions that benzene depletion is due solely to attack by hydroxyl radical (OH•), and that even high concentrations of ozone present in ambient atmospheres will not contribute significantly to the photooxidation of alkanes and aromatics, in general. A second-order rate of reaction of benzene with hydroxyl radicals of 0.85×10^{-9} l.mol^{-1}sec^{-1} has been obtained by Darnall *et al.* (1976) by averaging rates from smog chamber data by Hansen *et al.* (1975) and Davis *et al.* (1975). The temporal stability of benzene under actual atmospheric conditions is, as yet, unknown. Experiments performed in laboratory irradiation chambers are usually conducted for relatively short periods and cannot account for all of the meterological variables within a natural airshed.

71.4.3 Hydrolysis

No specific information pertaining to the hydrolysis of benzene under ambient conditions was found. The hydrolysis of benzene is an unlikely process under environmental conditions since nucleophilic attack of the aromatic ring by water or hydroxide ion will be impeded by its negative charge-density (Morrison and Boyd 1973).

71.4.4 Volatilization

The half-life with respect to volatilization from a water column one meter thick has been estimated by Mackay and Leinonen (1975) to be 4.81 hours for benzene at 25°C; at 10°C the half-life with respect to volatilization from the same depth of water has been estimated to be 5.03 hours. Mackay and Leinonen (1975) point out that for benzene the rates and half-lives of volatilization are insensitive to temperature and that temperature only affects the rate of volatilization significantly if the system is vapor-phase controlled. Some assumptions made in the estimation of rates of volatilization and half-lives were as follows: 1) the contaminant concentration is in solution rather than in suspended, colloidal, ionic, complexed, or adsorbed form; 2) the vapor is in equilibrium with the liquid at the interface; 3) the water diffusion or mixing is sufficiently fast so that the concentration at the interface approaches that of the bulk of the water; and 4) the rate of evaporation of water is negligibly affected by the presence of the contaminants.

Mackay and Leinonen (1975) point out that interpretation of the significance of the evaporative rate of compounds such as benzene from environmental waters using values calculated with a one-meter depth is dependent upon the type of environmental situation encountered. In situations where the water body is turbulent with frequent mixing between the surface layer and the bulk, as in a rapidly flowing shallow river or during white-capping on a lake or ocean, the evaporative rate would be more rapid than for depths greater than one meter or in quiescent water, as evidenced in a deep, slowly flowing river.

71.4.5 Sorption

Although no specific environmental sorption studies were found in the reviewed literature, the values of the log octanol/water partition coefficient found for benzene (log P=1.95, Leo et al. 1971; log P=2.13, Chiou et al. 1977) indicate that sorption processes may be significant for benzene under conditions of constant exposure. Presumably, benzene will be adsorbed by sedimentary organic material; the extent to which this possible adsorption will interfere with volatilization has not been considered.

71.4.6 Bioaccumulation

Neely et al. (1974) have shown that the bioaccumulation potential of a compound is related to the log octanol/water partition coefficient (log P) of the compound. The log P values obtained from the literature for benzene of 1.95 (Leo et al. 1971) and 2.13 (Chiou et al. 1977) indicate that the bioaccumulation potential of benzene by aquatic organisms at pollutant concentrations anticipated in environmental waters would probably be low.

71.4.7 Biotransformation and Biodegradation

Some species of soil bacteria have been demonstrated to be capable of utilizing benzene as the sole source of carbon (Zobell 1950; Gibson 1976; Claus and Walker 1964). A study by Walker and Colwell (1975), however, showed that petroleum-degrading bacteria isolated from the oil-polluted Colgate Creek of the Chesapeake Bay would only utilize benzene when present in combination with dodecane, or with dodecane and naphthalene. This utilization was suggested by Walker and Colwell (1975) to most likely occur as a result of co-oxidation or because of a lower concentration of benzene present than when petroleum-degrading bacteria were treated with benzene alone. Since measurable utilization of benzene at a 0.1% concentration occurred for more than 30% (68 of 200) of the pure cultures of hydrocarbon-utililizing bacteria, Walker and Colwell (1975) feel that the latter explanation cannot be excluded.

Gibson (1976) and Gibson *et al*. (1968) conducted experiments to determine the metabolic pathway involved in the microbial, oxidative degradation of benzene. Although the microorganism used in these experiments, *Pseudomonas putida*, could utilize benzene as the sole source of carbon and energy for growth, toluene served as a better substrate, and cells grown with toluene were used to investigate benzene metabolism. Gibson (1976) found that the initial reactions in the bacterial oxidation of aromatic hydrocarbons involved the formation of cis-dihydrodiols which undergo further oxidation to yield catechols. Gibson (1976) found that mammals, on the other hand, oxidize benzene to arene oxides which are hydrated to form trans-dihydrodiols prior to oxidation to yield catechols.

For several reasons, the view that only a few genera of bacteria such as *Pseudomonas* (Gibson 1976), and *Achromobacter* (Claus and Walker 1964) can utilize benzene as a sole carbon source may not be valid. The usual enrichment procedures for isolating such bacteria tend to select only those that grow rapidly. Vigorous growth in pure culture is a great advantage in biochemical studies but may not encompass all of the more important features of a natural habitat. A specific compound may in fact be readily metabolized in soil despite the failure to isolate single microbial species capable of using that compound as a sole carbon source (National Research Council 1977). On the other hand, the isolation of single species cabable of using a test compound as a sole carbon source must also be viewed with caution. An organism capable of using a test substrate as a sole carbon source in pure culture may not be able to assimilate the compound under natural conditions. Generally, the concentration of substrate used in pure culture studies is considerably higher than normally encountered in nature. As a result, the enzymes essential for biodegradation may not be induced under natural conditions. Further, pure culture studies rarely lead to useful degradation rate information (Howard and Durkin 1974).

Helfgott *et al*. (1977) report the refractory index (often referred to as the biorefractory index by other authors) of benzene to be 0.23

indicating that benzene is quite resistant to degradation. The refractory index of a compound as defined by Helfgott et al. (1977) is a parameter for estimating the biodegradability and treatability of organic materials found in and entering into the aquatic environment. Values for the refractory index normally range from 0.0 to 1.0. Refractory materials are defined as those materials having refractory index values (R.I.) of less than 0.6. According to Helfgott et al. (1977) such refractory compounds are not expected to degrade in an aerobic wastewater treatment system such as an activated sludge process and are expected to persist in natural water systems such as aquifers, rivers, and lakes. They suggest that the aromatic symmetry and electron delocalization of benzene are probably the factors which impart persistence to this compound. In a study by Thom and Agg (1975) benzene is listed as a synthetic organic chemical which should be degradable by biological sewage treatment provided that suitable acclimatization can be achieved.

71.5 Data Summary

Table 71-1 summarizes the aquatic fate information found for benzene. Volatilization appears to be the major transport process of benzene from the water column to the atmosphere. The atmospheric photooxidation of volatilized benzene probably subordinates all other fate processes. The reported rates of oxidation are atmospheric photooxidation rates based on smog chamber data. One half-life value and rate reported for the atmospheric photooxidation of benzene is based on the assumptions that benzene depletion is due solely to attack by hydroxyl radicals and that even high concentrations of ozone present in ambient atmospheres will not contribute significantly to the photooxidation of alkanes and aromatics, in general. Since benzene is relatively soluble in water, some benzene is expected to persist in the water column. That portion of benzene which persists in the water column would be expected to eventually biodegrade at a slow rate. The biodegradation of benzene would probably be enhanced by the presence of other hydrocarbons.

Table 71-1

Summary of Aquatic Fate of Benzene

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Since the ozone layer in the upper atmosphere effectively filters out wavelengths of light less than 290 nm, direct excitation of benzene in the aquatic or atmospheric environment is unlikely unless a substantial wavelength shift is caused by the media.	-	-	Low
Oxidation[a]	Direct oxidation of benzene in environmental waters is unlikely. Smog chamber data, however, indicate that benzene is photooxidized at a rapid rate in the atmosphere.	$0.85 \times 10^{-9} l.mol^{-1} sec^{-1}$ [d]	20 to 50 hours[b] 2.4 to 24 hours[c]	Medium
Hydrolysis	Probably not a significant fate process.	-	-	Medium
Volatilization	Probably the primary transport process.	-	4.81 hours[e]	Medium
Sorption	No specific information. The log P value for benzene indicates that sorption may occur.	-	-	Low
Bioaccumulation	The log P value of benzene indicates a low bioaccumulation potential for benzene.	-	-	Low
Biotransformation/ Biodegradation	Benzene can be utilized as the sole source of carbon by several microorganisms and is probably biodegradable at a slow rate.	-	-	Medium

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a. The predominant environmental process which is thought to determine the fate of the compound.

b. This half-life is calculated from the half-conversion time for benzene based on smog chamber data by Altshuller et al. (1962) and the table of relative reactivities given by Laity et al. (1973).

c. This half-life is the estimated half-life value proposed by Darnall et al. (1976) and is based on the assumption that benzene depletion is due solely to attack by hydroxyl radical.

d. This second-order rate of reaction of benzene with hydroxyl radicals has been obtained by Darnall et al. (1976) by averaging rates from smog chamber data by Hansen et al. (1975) and Davis et al. (1975).

e. This is the half-life estimated by Mackay and Leinonen (1975) for volatilization of benzene from a water column one meter thick at 25°C. This rate of volatilization varies with the environmental situation encountered.

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72. CHLOROBENZENE

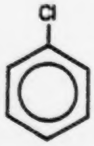
72.1 Statement of Probable Fate

Based on the information found, it is not possible to determine the predominant aquatic fate of chlorobenzene. There is some experimental evidence indicating that volatilized chlorobenzene will undergo atmospheric photooxidation in the presence of nitric oxide. The extent to which such photooxidation will occur at chlorobenzene concentrations prevalent in the atmospheric environment in the presence of nitric oxide, as well as other free radical initiators, is unknown. Information found concerning the biodegradation potential of chlorobenzene indicates that this compound, being very persistent, will probably eventually biodegrade, but not at a substantial rate unless the microorganisms present are already growing on another hydrocarbon source.

Chlorobenzene has a high affinity for lipophilic materials, and it also is reported to have a relatively low solubility at temperatures anticipated to be prevalent in most ambient waters. Consequently, sorption, bioaccumulation, and volatilization are expected to be competing processes. The rate at which each of these competing processes occur will determine which fate is predominant for chlorobenzene in the aquatic environment. Should volatilization occur at a more rapid rate than sorption or bioaccumulation, then atmospheric processes would be expected to regulate the fate of chlorobenzene. On the other hand, should sorption and bioaccumulation occur more rapidly than volatilization, biodegradation of chlorobenzene by aquatic microorganisms would be anticipated to regulate the fate of this compound.

72.2 Identification

Chlorobenzene has been detected in finished drinking water, in ground water, in uncontaminated upland water, in waters contaminated by either industrial, municipal, or agricultural wastes (U.S. Environmental Protection Agency 1975), and in the atmosphere (Ware and West 1977). The chemical structure of chlorobenzene is shown below.



Chlorobenzene

CAS NO. 108-90-7
TSL NO. CZ 01750

Alternate Names

Monochlorobenzene
Benzene Chloride

72.3 Physical Properties

The general physical properties of chlorobenzene are given below.

Molecular weight (Verschueren 1977)	112.56
Melting point (Verschueren 1977)	-45°C
Boiling point at 760 torr (Verschueren 1977)	132°C
Vapor pressure at 20°C	*
Solubility in water	**
Log octanol/water partition coefficient (Leo _et_ _al_. 1971; Chiou _et_ _al_. 1977)	2.84

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*Values for the vapor pressure of chlorobenzene in water were reported to be 8.8 torr at 20°C (Verschueren 1977) and were calculated to be 11.72 torr at 20°C from the table of vapor pressures, critical temperatures and critical pressures of organic compounds in Weast (1973).

**Values for the solubility of chlorobenzene in water were reported to be 500 mg/l at 20°C (Verschueren 1977), 488 mg/l at 25°C (Mardsen and Marr 1963), and 448 mg/l at 30°C (Chiou _et_ _al_. 1977).

72.4 Summary of Fate Data

72.4.1 Photolysis

No specific information pertaining to the direct photolysis of chlorobenzene in the aqueous or atmospheric environments under ambient conditions was found.

72.4.2 Oxidation

No specific information pertaining to the oxidation of chlorobenzene in the aqueous environment under ambient conditions was found.

Dilling _et_ _al_. (1976) studied the photodecomposition rate of chlorobenzene under simulated atmospheric conditions. The reactor was a waterjacketed Pyrex cylinder maintained at 27 ± 1°C and 35% relative humidity. The ultraviolet light sources were two General Electric 275-Wreflector sunlamps, each of which had a short wavelength cutoff of 290 nm. Chlorobenzene decomposed relatively slowly when compared to other chlorinated compounds studied. In the presence of nitric oxide, a probable reaction initiator, chlorobenzene, at a concentration of 10 mg/1, underwent 43% reaction in 7.5 hours; this corresponds to an estimated half-life of 8.7 hours. No photodecomposition products were reported. For comparison, the estimated half-life of benzene proposed by Darnall et al. (1976) was 2.4 to 24 hours. Using the half-conversion time of m-xylene and 1,3,5-trimethylbenzene, which was reported to be somewhat less than four hours (Altshuller et al. 1962), and the table of relative reactivities given by Laity et al. (1973), the corresponding range for the half-conversion time for benzene was inferred to be approximately 20 to 50 hours. Due to decreased susceptibility to electrophilic attack, chlorobenzene would be anticipated to have a longer half-life than benzene under similar conditions of exposure. Because the experimental procedure of Dilling et al. (1976) is different from the hypothetical conditions used for the theoretical calculation of Darnall et al. (1976) the results cannot be quantitatively compared. However, they do show that chlorobenzene will undergo photolysis over a defined range of times. In addition, experiments of the type carried out by Dilling et al. (1976) should, for accuracy, be carried out for at least 2 or 3 half-times.

72.4.3 Hydrolysis

Chlorobenzene, being an aryl halide, will undergo nucleophilic substitution only with extreme difficulty. For example, Morrison and Boyd (1973) report that chlorobenzene is converted into phenol by aqueous sodium hydroxide only at temperatures over 300°C. Consequently, hydrolysis of chlorobenzene under environmental conditions would not be expected to occur.

72.4.4 Volatilization

Available data on chlorobenzene indicate that this compound probably volatilizes from the water column to the atmosphere at a relatively rapid rate. Garrison and Hill (1972) reported that at 300 mg/1 of chlorobenzene volatilized almost completely (less than 1 mg/1 chlorobenzene remained) from aerated distilled water in less than four hours. The same concentration of chlorobenzene volatilized almost completely (less than 1 mg/1 chlorobenzene remained) from unaerated distilled water in less than 3 days. No further details of this experiment were reported. Assuming a first order process and also assuming that volatilization is the only removal process operating (i.e., no gas-stripping and negligible adsorption onto container walls), the data of Garrison and Hill (1972) yield estimates of about 0.5 hours and 9 hours for evaporative half-lives of chlorobenzene in water under conditions of aeration and quiescence, respectively. Because of the limited data on experimental conditions, it is difficult to interpret the effect of aeration on the rate of evaporation. Furthermore, because of the possibility of air-stripping during aeration, it is concluded that the 0.5 hour value is not a valid evaporative half-life for chlorobenzene in agitated water. The value of 9 hours appears to be valid for the non-agitated case.

According to Mackay and Wolkoff (1973) the rate of evaporation of pollutants having a low solubility in water can be quite rapid even though these compounds often have a high molecular weight and a low vapor pressure, and should, on these bases, evaporate slowly. Mackay and Wolkoff (1973) contend that these compounds often have high activity coefficients in water which cause unexpectedly high partial vapor pressures at equilibrium and thus high rates of evaporation. Although chlorobenzene, which has a reasonably low solubility in water of 488 mg/l at 25°C (Mardsen and Marr 1963), was not mentioned specifically, other chlorinated hydrocarbons having a low solubility in water were predicted to have relatively rapid rates of evaporation. Presumably, chlorobenzene would have a rate of evaporation similar to compounds having vapor pressure and solubility values approximately equal to those values for chlorobenzene.

The published values for the vapor pressure (Weast 1973) and solubility (Mardsen and Marr 1963) of chlorobenzene in water at 25°C were used to compute the Henry constant as being approximately 3.56×10^{-3} atmos. m^3/mole. This constant for chlorobenzene may be compared to the value of 3.51×10^{-3} atmos m^3/mole predicted for Aroclor 1248 at 25°C (Mackay and Leinonen 1975). In the case of Aroclor 1248, the half-life for evaporation from a water column one meter thick was estimated by Mackay and Leinonen (1975) to be 9.53 hours at 25°C. An estimate of the corresponding half-life for evaporation of chlorobenzene under the same conditions would presumably be of the same order, approximately 10 to 11 hours, or close to the value of about 9 hours discussed previously.

The interpretation of the environmental significance of the rate of evaporation of chlorobenzene based on calculations involving an assumed depth of one meter is dependent upon the type of environmental situation encountered. In situations where the water body is turbulent with frequent mixing between the surface layer and the bulk, as in a rapidly flowing shallow river, or during white-capping on a lake or ocean, the rate of evaporation would be more rapid than for depths greater than one meter or in quiescent water, as exists in a deep, slowly flowing river.

72.4.5 Sorption

Although no specific environmental sorption studies were found in the literature, the values of the log octanol/water partition coefficient found for chlorobenzene (log P = 2.84, Leo et al. 1971; Chiou et al. 1977) indicate that sorption processes may be substantial for chlorobenzene at pollutant concentrations anticipated in environmental waters. Presumably, chlorobenzene will be adsorbed by sedimentary organic material; the extent to which this possible adsorption will interfere with volatilization has not been considered.

72.4.6 Bioaccumulation

Chlorobenzene was studied for its bioaccumulation potential in a model aquatic ecosystem developed by Lu and Metcalf (1975). This aquatic ecosystem was devised for studying relatively volatile organic compounds and simulating direct discharge of chemical wastes. A 3-liter flask containing members of an aquatic food chain, including daphnia, mosquito larvae, snails, mosquito fish, and green filamentous algae, was maintained at 80°F with 12 hours daylight exposure. Radiolabelled derivatives were added to the flask in concentrations of 0.01 to 0.1 ppm. After 48 hours, the experiment was terminated.

The contaminative efficacy of chlorobenzene was evaluated by determining the quantitative distribution of the radioactivity in the organisms, water, and air of the model aquatic ecosystem. Chlorobenzene was found to be a highly persistent compound, as demonstrated by the ecological magnification (EM) values (often referred to as the bioconcentration or bioaccumulation factors by other authors) of 645 in fish, 1292 in mosquito larva, 1313 in snail, 2789 in daphnia, and 4185 in alga. Lu and Metcalf (1975) define ecological magnification as the ratio of the concentration of the parent compound in an organism to the concentration in the water. Hydroxylation served as the predominant detoxification mechanism of chlorobenzene by all of the organisms in the model aquatic food chain except filamentous green alga, *Oedogonium cardiacum*. Hydroxylation of chlorobenzene to o- and p-chlorophenol and to 4-chlorocatechol was found in mosquito larva and in water extracts.

In addition to experimental evidence, there is empirical evidence that chlorobenzene has a high potential for bioaccumulation in organisms. Neely et al. (1974) and Lu and Metcalf (1975) have shown that the log octanol/water partition coefficient (log P) correlates well with the ability of a compound to accumulate in the lipids of tissues of living organisms. The log P value of 2.84 (Leo et al. 1971; Chiou et al. 1977) indicates that bioaccumulation of chlorobenzene by aquatic organisms at pollutant concentrations anticipated in environmental waters will probably occur.

72.4.7 Biotransformation and Biodegradation

Some species of soil bacteria have been demonstrated to be capable of obtaining their energy and carbon requirements from chlorobenzene (Matthews 1924). A study by Gibson *et al*. (1968), however, indicated that the microorganism *Pseudomonas putida* could oxidize chlorobenzene only when it was already growing on an aromatic hydrocarbon source. In this study, cultures of *Pseudomonas putida* were initially grown on toluene as the sole source of carbon for 15 hours and were subsequently grown on chlorobenzene for up to 20 hours. This oxidative degradation of chlorobenzene by *Pseudomonas putida* resulted in the formation of 3-chlorocatechol (Gibson *et al*. 1968).

In a study by Garrison and Hill (1972), chlorobenzene was exposed to aerated mixed cultures of aerobic microorganisms to test their resistance to microbial action. Garrison and Hill (1972) reported that chlorobenzene volatilized completely from these aerated cultures in less than one day. No other information on this particular study was given.

In a report by Heukelekian and Rand (1955) BOD (Biochemical Oxygen Demand) data on pure compounds were compiled and assembled into broad groups on the basis of certain chemical similarities. The BOD values were expressed as grams per gram of chemical tested at 20°C. Most of the data reported have BOD values based on a 5-day incubation period, although there were some BOD values based on an incubation period of 10 days or based on ultimate values. From the reported data, it appears that the presence of a chlorine atom on a benzene ring results in a BOD value lower than that of benzene itself. For comparison, the BOD of benzene was reported as 1.20 g/g after a 10-day incubation period whereas the BOD of chlorobenzene was reported to be 0.03 g/g after a 5-day incubation period. This decrease in BOD value as a result of the presence of a chlorine atom on the benzene ring indicates an increased resistance to microbial attack. Although the difference in the incubation time for benzene and chlorobenzene could account to some degree for the difference in BOD values for the two compounds, Alexander and Lustigman (1966) also found that the presence of a chlorine atom on the benzene ring retarded the rate of biodegradation.

Lu and Metcalf (1975) reported values for the biodegradability index of chlorobenzene ranging from 0.014 to 0.063 in organisms found in a model aquatic ecosystem. The biodegradability index is defined as the ratio of polar products of degradation to the non-polar products. A low value for the biodegradability index indicates that a compound resists biodegradation. Comparison of the biodegradability index of chlorobenzene with that of some more widely studied persistent pollutants such as DDT and aldrin, give a better idea of the significance of these values. Lu and Metcalf (1975) reported a biodegradability index for DDT of 0.012 in mosquito fish compared to a value of 0.015 for aldrin, and 0.014 for chlorobenzene.

72.4.8 Other Reactions

In an investigation by Carlson *et al.* (1975), monosubstituted aromatics were exposed to low concentrations of aqueous chlorine (7 x 10^{-4}M) for 20 minutes at varying pH conditions to determine the extent of chlorine incorporation into aromatic compounds. Chlorine, being an electrophile, was found to be more slowly incorporated into aromatic compounds containing deactivating groups such as chloro, nitro, nitrile, and carbonyl than into aromatic compounds containing activating groups such as hydroxyl, ether, amine derivatives, or alkyl. For comparison, when chlorobenzene, a compound containing a ring-deactivating group, and phenol, a compound containing a ring-activating group, were exposed at pH 3 to 7 x 10^{-4}M aqueous chlorine for 20 minutes, the chlorine uptake was 1.8 ± 0.1% and 97.8 ± 0.1%, respectively. Chlorobenzene was not chlorinated at higher pH. Since the typical range of pH found during the course of most water treatment processes is 5 to 9, there is a low probability of forming higher chlorinated benzenes from reactions of chlorine and chlorobenzene.

72.5 Data Summary

There is not enough environmentally significant information on photolysis, oxidation, or sorption processes to be able to predict the aquatic fate of chlorobenzene. Chlorobenzene has a high affinity for lipophilic materials, and it is also reported to have a relatively low solubility at temperatures expected to prevail in most ambient waters. Consequently, sorption, bioaccumulation, and volatilization are expected to be competing processes. The rate at which each of these competing processes occur will dictate which fate is predominant for chlorobenzene in the aquatic environment. These data are summarized in Table 72-1.

Table 72-1

Summary of Aquatic Fate of Chlorobenzene

Environmental Process[a]	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	No information found.	-	-	Low
Oxidation	No information was found concerning the oxidation of chlorobenzene in ambient waters. Experimental evidence indicates that volatilized chlorobenzene will undergo atmospheric photooxidation in the presence of nitric oxide. The extent to which photooxidation will occur at chlorobenzene concentrations prevalent in the atmospheric environment in the presence of nitric oxide or other initiators in unknown.	-	8.7 hours[b]	Low
Hydrolysis	Chlorobenzene probably will not hydrolyze in ambient waters due to the extreme difficulty with which aryl halides undergo nucleophilic substitution.	-	-	Medium
Volatilization	This compound probably volatilizes from the water column to the atmosphere at a relatively rapid rate.	-	9 hours[c] 10 or 11 hours[d]	Medium
Sorption	The high log P value found for chlorobenzene indicates that sorption processes may be substantial for chlorobenzene at pollutant concentrations anticipated in environmental waters.	-	-	Low
Bioaccumulation	Experimental and empirical evidence indicates that chlorobenzene has an intermediate potential for bioaccumulation in the lipids of tissues of living organisms.		-	Medium
Biotransformation/ Biodegradation	Information found concerning the biodegradation potential of chlorobenzene indicates that this compound will probably eventually biodegrade, but not at a substantial rate unless the microorganisms present are already growing on another hydrocarbon source.	-	-	Medium

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. This half-life is the estimated half-life based on the experimental results and conditions of Dilling et al. (1976) and probably does not reflect the photooxidation half-life of chlorobenzene under environmental conditions.

c. This half-life is the estimated half-life based on the experimental results and conditions of Garrison and Hill (1972) in unaerated distilled water.

d. This half-life is based on the calculated Henry constant of chlorobenzene which is of the same order as the Henry constant predicted for Aroclor 1248 at 25°C by Mackay and Leinonen (1975). Since the half-life for evaporation of Aroclor 1248 from a water column one meter thick was estimated by Mackay and Leinonen (1975) to be 9.53 hours at 25°C, the half-life for evaporation of chlorobenzene under the same conditions was assumed to be only slightly longer.

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73. 1,2-DICHLOROBENZENE (o-DICHLOROBENZENE)

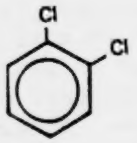
73.1 Statement of Probable Fate

Based on the information found, it is not possible to determine the predominant aquatic fate of 1,2-dichlorobenzene. There is some evidence that dichlorobenzenes in general are reactive toward hydroxyl radicals in air with a half-life of approximately three days. Products and further details of such photooxidation reactions, however, were not indicated. Information concerning the biodegradation potential of 1,2-dichlorobenzene indicates that this compound is very persistent and will probably, at best, be biodegraded very slowly by microorganisms already growing on another hydrocarbon source.

1,2-Dichlorobenzene has a high affinity for lipophilic materials and it is reported to have a relatively low vapor pressure and low aqueous solubility at ambient temperatures. Consequently, sorption, bioaccumulation, and volatilization are expected to be competing processes. The rate at which each of these competing processes occur will determine which fate is predominant for 1,2-dichlorobenzene in the aquatic environment. Should volatilization occur at a more rapid rate than sorption or bioaccumulation, then atmospheric processes would be expected to regulate the fate of 1,2-dichlorobenzene. On the other hand, should sorption and bioaccumulation occur more rapidly than volatilization, biodegradation of 1,2-dichlorobenzene by aquatic microorganisms would be anticipated to regulate the fate of this compound.

73.2 Identification

1,2-Dichlorobenzene has been detected in finished drinking water, in superchlorinated municipal wastewaters, in ground water (U.S. Environmental Protection Agency 1975), in wastewater effluent (Glaze and Henderson 1975), and in the atmosphere (Ware and West 1977). The chemical structure of 1,2-dichlorobenzene is shown below.



1,2-Dichlorobenzene

CAS NO. 95-50-1
TSL NO. CZ 45000

Alternate Names

o-Dichlorobenzene
Orthodichlorobenzene
Dowtherm E

73.3 Physical Properties

The general physical properties of 1,2-dichlorobenzene are given below.

Molecular weight (Weast 1977)	147.01
Melting point (Weast 1977)	-17.0°C
Boiling point at 760 torr (Weast 1977)	180.5°C
Vapor pressure at 25°C	1.5 torr*
Solubility in water at 25°C (Verschueren 1977)	145 mg/1
Log octanol/water partition coefficient (Leo *et al*. 1971)	3.38

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*Values for the vapor pressure of 1,2-dichlorobenzene in water were reported to be 1.5 torr at 25°C (Verschueren 1977) and were calculated to be 1.45 torr from the table of vapor pressures, critical temperatures and critical pressures of organic compounds in Weast (1973).

73.4 Summary of Fate Data

73.4.1 Photolysis

No specific information pertaining to the direct photolysis of 1,2-dichlorobenzene in the aquatic or atmospheric environments was found.

73.4.2 Oxidation

According to Ware and West (1977) 1,2-dichlorobenzene is resistant to autooxidation by the peroxy radical ($RO_2\cdot$) in water. No more details of this phenomenon were reported. Dichlorobenzenes in general were reported by Ware and West (1977) to be reactive toward hydroxyl radicals ($OH\cdot$) in air with a half-life of approximately three days. Products and further details of such photooxidation reactions were not indicated. 1,2-Dichlorobenzene specifically was reported by Ware and West (1977) to be resistant to autooxidation by ozone in air.

73.4.3 Hydrolysis

No specific information pertaining to the hydrolysis of 1,2-dichlorobenzene has been found. Although Ware and West (1977) report that the inductive electronegative effect of halogen substitutents on an aromatic ring facilitates attack by nucleophiles such as OH^-, Morrison and Boyd (1973) report that aryl halides are characterized by very low reactivity toward nucleophilic reagents such as OH^-.

As an example of the difficulty with which aryl halides undergo nucleophilic substitution, the conditions necessary for the nucleophilic substitution of hexachlorobenzene to a pentachlorophenyl derivative were reported by Patai (1973) to be the presence of aqueous ammonia at a temperature of at least 250°C. On this basis, 1,2-dichlorobenzene, being less chlorinated and, consequently, less easily attacked by nucleophiles than hexachlorobenzene, would not be expected to undergo hydrolysis at an appreciable rate under environmental conditions.

73.4.4 Volatilization

Available data on 1,2-dichlorobenzene indicate that this compound probably volatilizes from the water column to the atmosphere at a relatively rapid rate. Garrison and Hill (1972) reported that a 100 mg/l concentration of 1,2-dichlorobenzene volatilized almost completely (less than 1 mg/l of 1,2-dichlorobenzene remained) from aerated distilled water in less than 4 hours. The same concentration of 1,2-dichlorobenzene volatilized almost completely (less than 1 mg/l of 1,2-dichlorobenzene remained) from unaerated distilled water in less than 3 days. No further details of this experiment were reported. The data of Garrison and Hill (1972) can be used to calculate approximate values for evaporative half-lives. For the aerated solution, the calculated half-life is less than 30 minutes; however, since the aeration probably caused air-stripping of the 1,2-dichlorobenzene, this value is not representative of an evaporative half-life under conditions of agitation. The data for unaerated conditions, apparently close to quiescence, correspond to a half-life of less than about nine hours.

According to Mackay and Wolkoff (1973) the rate of evaporation of pollutants having a low solubility in water can be quite rapid even though these compounds often have a high molecular weight and a low vapor pressure, and should, on these bases, evaporate slowly. Mackay and Wolkoff (1973) contend that these compounds often have high activity coefficients in water which cause unexpectedly high equilibrium partial vapor pressures and thus high rates of evaporation. Although 1,2-dichlorobenzene was not mentioned specifically, other chlorinated hydrocarbons having relatively low solubility in water were predicted to have somewhat rapid rates of evaporation.

The published value for the vapor pressure (Verschueren 1977) and solubility in water (Verschueren 1977) of 1,2-dichlorobenzene at 25°C were used to compute the Henry constant as being approximately 1.99 x 10^{-3} atmos. m^3/mole which may be compared to the value of 1.55 x 10^{-3} atmos. m^3/mole predicted for biphenyl at 25°C (Mackay and Leinonen 1975). In the case of biphenyl, the half-life for evaporation from a water column one meter thick was estimated by Mackay and Leinonen (1975) to be 7.52 hours at 25°C. An estimate of the corresponding half-life for evaporation of 1,2-dichlorobenzene under the same conditions would presumably be of the same order, at most, approximately 8 or 9 hours. Mackay and Leinonen (1975) point out that interpretation of the environmental significance of the rate of evaporation of compounds such as 1,2-dichlorobenzene from environmental waters using values calculated at 1 meter depth is dependent upon the type of environmental situation encountered. In situations where the water body is turbulent with frequent mixing between the surface layer and the bulk, as in a rapidly flowing shallow river or during white-capping on a lake or ocean, the rate of evaporation would be more rapid than for depths greater than 1 meter or in quiescent water, as exists in a deep, slowly flowing river.

73.4.5 Sorption

Although no specific environmental sorption studies were found in the literature, the value of the log octanol/water partition coefficient for 1,2-dichlorobenzene (log P = 3.38, Leo *et al*. 1971) indicates that sorption processes may be substantial for 1,2-dichlorobenzene at pollutant concentrations anticipated in environmental waters. Presumably, 1,2-dichlorobenzene will be adsorbed by sedimentary organic material; the extent to which this possible adsorption will interfere with volatilization has not been considered.

73.4.6 Bioaccumulation

Although no experimental evidence of the bioaccumulation potential of 1,2-dichlorobenzene was found, there is indirect evidence that 1,2-dichlorobenzene has a high potential for bioaccumulation in aquatic organisms. Neely *et al*. (1974) and Lu and Metcalf (1975) have shown that the log octanol/water partition coefficient (log P) correlates well with the ability of a compound to accumulate in the lipids of tissues of living organisms. Furthermore, the incorporation of chlorine into an organic molecule increases its lipophilic character resulting in an increased bioaccumulation potential (Kopperman *et al*. 1976). For comparison, chlorobenzene, a compound containing only one chlorine atom, and 1,2-dichlorobenzene, a compound having two chlorine atoms, have log P values of 2.84 (Leo *et al*. 1971; Chiou *et al*. 1977) and 3.38 (Leo *et al*. 1971), respectively. Since it has been established experimentally that chlorobenzene bioaccumulates in aquatic organisms (Lu and Metcalf 1975), 1,2-dichlorobenzene, would be expected to be bioaccumulated by aquatic organisms at least as much as chlorobenzene.

73.4.7 Biotransformation and Biodegradation

According to Ware and West (1977), the more highly halogenated a compound becomes, the more resistant it is to biodegradation. Experimental (Lu and Metcalf 1975) as well as empirical evidence (Leo *et al.* 1971; Chiou *et al.* 1977) has been found indicating that chlorobenzene is a persistent chemical and is not readily biodegraded unless the microorganisms present are already growing on another hydrocarbon source. Furthermore, Alexander and Lustigman (1966) found that the presence of a chlorine atom on the benzene ring retarded the rate of biodegradation. On these bases, 1,2-dichlorobenzene, being more highly chlorinated than chlorobenzene, would presumably biodegrade at least as slowly as chlorobenzene under the same conditions of exposure to microorganisms.

Evidence that 1,2-dichlorobenzene is a persistent chemical is presented in a study by Thom and Agg (1975), which lists 1,2-dichlorobenzene as a synthetic organic chemical which is unlikely to be removed during biological sewage treatment even after prolonged exposure of the biota. In contrast, Thom and Agg (1975) list chlorobenzene, a compound with one less chlorine atom than 1,2-dichlorobenzene, as a synthetic organic chemical which should be degradable by biological sewage treatment provided that suitable acclimatization can be achieved. Based upon inference 1,2-dichlorobenzene should be resistent to biodegradation; but in the absence of solid experimental evidence, no definitive conclusion can be reached.

73.5 Data Summary

There is not enough environmentally significant information on photolysis, oxidation, sorption, or biodegradation processes to be able to predict the aquatic fate of 1,2-dichlorobenzene. 1,2-Dichlorobenzene has a high affinity for lipophilic materials and it is reported to have a relatively low vapor pressure and low solubility at temperatures expected to prevail in most ambient waters. Consequently, sorption, bioaccumulation, and volatilization are expected to be competing processes. The rate at which each of these competing processes occur will dictate which fate is predominant for 1,2-dichlorobenzene in the aquatic environment. These data are summarized in Table 73-1.

Table 73-1

Summary of Aquatic Fate of 1,2-Dichlorobenzene

Environmental Process[a]	Summary Statement	Rate	Half-Life $(t_{1/2})$	Confidence of Data
Photolysis	No information found	-	-	Low
Oxidation	1,2-Dichlorobenzene is reported to be resistant to autooxidation by the peroxy radical ($RO_2\cdot$) in water. Dichlorobenzenes were reported to be reactive toward hydroxyl radicals ($OH\cdot$) in air.	-	~3 days[b]	Low
Hydrolysis	1,2-Dichlorobenzene will probably not hydrolyze in ambient waters due to the extreme difficulty with which aryl halides undergo nucleophilic substitution.	-	-	Medium
Volatilization	This compound probably volatilizes from the water column to the atmosphere at a relatively rapid rate.	-	∿8 or 9 hours[c] less than 9 hours[d]	Medium
Sorption	The high log P value found for 1,2-dichlorobenzene indicates that sorption processes may be sustantial for this compound at pollutant concentrations anticipated in environmental waters.	-	-	Low
Bioaccumulation	Empirical evidence indicates that 1,2-dichlorobenzene will bioaccumulate in the lipids of tissues of living organisms.	-	-	Low
Biotransformation/ Biodegradation	Will biodegrade, at best, at a very slow rate.	-	-	Low

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. This half-life is the reported half-life of dichlorobenzene toward hydroxyl radicals in air cited in Ware and West (1977).

c. This half-life is based on the calculated Henry constant of 1,2-dichlorobenzene which is of the same order as the Henry constant predicted for biphenyl at 25°C by Mackay and Leinonen (1975). Since the half-life for evaporation of biphenyl from a water column one meter thick was estimated by Mackay and Leinonen to be 7.52 hours at 25°C, the half-life for evaporation of 1,2-dichlorobenzene under the same conditions was assumed to be of the same order, at most, approximately 8 or 9 hours.

d. This half-life is the estimated half-life based on the experimental results and conditions of Garrison and Hill (1972) in unaerated distilled water.

73.6 Literature Cited

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74. 1,3-DICHLOROBENZENE (m-DICHLOROBENZENE)

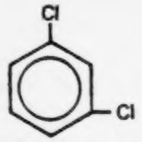
74.1 Statement of Probable Fate

Based on the information found, it is not possible to determine the predominant aquatic fate of 1,3-dichlorobenzene. The probable aquatic fate of this compound can only be inferred from information available on its more thoroughly studied structural isomers, 1,2- and 1,4-dichlorobenzene, and from information available on dichlorobenzenes in general. There is some evidence that dichlorobenzenes are reactive toward hydroxyl radicals in air with a half-life of approximately three days. Products and further details of such photooxidation reactions, however, were not indicated. Information concerning the biodegradation potential of 1,3-dichlorobenzene indicates that this compound is very persistent and will probably, at best, be biodegraded only very slowly by microorganisms already growing on another hydrocarbon source.

1,3-Dichlorobenzene has a high affinity for lipophilic materials, a relatively low vapor pressure, and low aqueous solubility at ambient temperatures. Consequently, sorption, bioaccumulation, and volatilization are expected to be competing processes. The rate at which each of these competing processes occurs will determine which fate is predominant for 1,3-dichlorobenzene in the aquatic environment. Should volatilization occur at a more rapid rate than sorption or bioaccumulation, then atmospheric processes would be expected to regulate the fate of 1,3-dichlorobenzene. On the other hand, should sorption and bioaccumulation occur more rapidly than volatilization, biodegradation of 1,3-dichlorobenzene by aquatic microorganisms would be anticipated to control the fate of this compound.

74.2 Identification

1,3-Dichlorobenzene has been detected in drinking water and ground water (U.S. Environmental Protection Agency 1975). The chemical structure of 1,3-dichlorobenzene is shown below.



1,3-Dichlorobenzene

CAS NO. 541-73-1
TSL NO. None Assigned

Alternate Names

m-Dichlorobenzene
Metadichlorobenzene

74.3 Physical Properties

The general physical properties of 1,3-dichlorobenzene are given below.

Molecular weight (Weast 1977)	147.01
Melting point (Weast 1977)	-24.7°C
Boiling point at 760 torr (Weast 1977)	173°C
Vapor pressure at 25°C (Weast 1973)	2.28 torr*
Solubility in water at 25°C (Verschueren 1977)	123 mg/l
Log octanol/water partition coefficient (Leo *et al*. 1971)	3.38

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*This vapor pressure was calculated from the table of vapor pressures, critical temperatures and critical pressures of organic compounds in Weast (1973).

74.4 Summary of Fate Data

74.4.1 Photolysis

No specific information pertaining to the direct photolysis of 1,3-dichlorobenzene in the aquatic or atmospheric environments was found.

74.4.2 Oxidation

No specific information pertaining to the oxidation of 1,3-dichlorobenzene in ambient waters was found.

Dichlorobenzenes in general were reported by Ware and West (1977) to be reactive toward hydroxyl radicals (OH•) in air with a half-life of approximately three days. Products and further details of such photooxidation reactions were not indicated.

74.4.3 Hydrolysis

No specific information pertaining to the hydrolysis of 1,3-dichlorobenzene in ambient waters was found. Although Ware and West (1977) report that the inductive electronegative effect of halogen substituents on the benzene ring facilitates attack by nucleophiles such as OH$^-$, Morrison and Boyd (1973) report that aryl halides will undergo nucleophilic substitution only with extreme difficulty. For example, Patai (1973) reported that the minimum conditions necessary for the nucleophilic substitution of hexachlorobenzene to a pentachlorophenyl derivative were the presence of aqueous ammonia and a temperature of at least 250°C. On these bases, 1,3-dichlorobenzene, being less chlorinated and, consequently, less easily attacked by nucleophiles than hexachlorobenzene, would not be anticipated to undergo hydrolysis at an appreciable rate under environmental conditions.

74.4.4 Volatilization

Garrison and Hill (1972) found that chlorobenzene, 1,2-dichlorobenzene, 1,4-dichlorobenzene, and 1,2,4-trichlorobenzene volatilized almost completely (less than one mg/l of the compounds remained) from aerated distilled water in less than four hours. Initial concentrations of the compounds were 300 mg/l, 100 mg/l, 300 mg/l, and 100 mg/l, respectively. The same concentrations of the four chlorinated benzenes volatilized from unaerated distilled water in less than three days. 1,2,4-Trichlorobenzene disappeared from unaerated distilled water in less than two days. Presumably, 1,3-dichlorobenzene under similar conditions would volatilize at a similar rate.

According to Mackay and Wolkoff (1973) the rate of evaporation of pollutants having a low solubility in water can be quite rapid even though these compounds often have a high molecular weight and a low vapor pressure, and should, on these bases, evaporate slowly. Mackay and Wolkoff (1973) contend that these compounds often have high activity coefficients in water which cause unexpectedly high equilibrium partial vapor pressures and thus high rates of evaporation. Although 1,3-dichlorobenzene, which has a reasonably low vapor pressure of 2.28 torr (calculated from Weast 1973) and a low solubility in water of 123 mg/l at 25°C (Verschueren 1977) was not mentioned specifically, other chlorinated hydrocarbons having a low solubility in water and a low vapor pressure were predicted to have relatively rapid rates of evaporation. Presumably, 1,3-dichlorobenzene would have a rate of evaporation similar to these chlorinated compounds having vapor pressure and solubility values approximately equal to those values for 1,3-dichlorobenzene.

The calculated value for the vapor pressure (Weast 1973) and the published value for the solubility in water (Verschueren 1977) of 1,3-dichlorobenzene at 25°C were used to compute the Henry constant as being approximately 3.58×10^{-3} atmos. m^3/mole, which may be compared to the value of 3.51×10^{-3} atmos. m^3/mole predicted for Aroclor 1248 at 25°C (Mackay and Leinonen 1975). In the case of Aroclor 1248, the half-life for evaporation from a water column one meter thick was estimated by Mackay and Leinonen (1975) to be 9.53 hours at 25°C. The corresponding half-life for evaporation of 1,3-dichlorobenzene under the same conditions would presumably be of the same order, at most, approximately 10 or 11 hours. Mackay and Leinonen (1975) point out that interpretation of the environmental significance of the rate of evaporation of compounds such as 1,3-dichlorobenzene from environmental waters using values calculated at 1 meter depth is dependent upon the type of environmental situation encountered. In situations where the water body is turbulent with frequent mixing between the surface layer and the bulk, as in a rapidly flowing shallow river or during white-capping on a lake or ocean, the rate of evaporation would be more rapid than for depths greater than 1 meter or in quiescent water, as evidenced in a deep, slowly flowing river.

74.4.5 Sorption

Although no specific environmental sorption studies were found in the literature, the value of the log octanol/water partition coefficient found for 1,3-dichlorobenzene (log P = 3.38, Leo et al. 1971) indicates that sorption processes may be substantial for 1,3-dichlorobenzene at pollutant concentrations anticipated in environmental waters. Presumably, 1,3-dichlorobenzene will be adsorbed by sedimentary organic material; the extent to which this possible adsorption will interfere with volatilization has not been considered.

74.4.6 Bioaccumulation

Although no experimental evidence of the bioaccumulation potential of 1,3-dichlorobenzene was found, there is empirical evidence that 1,3-dichlorobenzene has a high potential for bioaccumulation in aquatic organisms. Neely et al. (1974) and Lu and Metcalf (1975) have shown that the log octanol/water partition coefficient (log P) correlates well with the ability of a compound to accumulate in the lipids of tissues of living organisms. Furthermore, the incorporation of chlorine into an organic molecule increases its lipophilic character resulting in an increased bioaccumulation potential (Kopperman et al. 1976). For comparison, chlorobenzene, a compound containing only one chlorine atom, and 1,3-dichlorobenzene, a compound having two chlorine atoms, have log P values of 2.84 (Leo et al. 1971; Chiou et al. 1977) and 3.38 (Leo et al. 1971), respectively. Since it has been established experimentally that chlorobenzene bioaccumulates in aquatic organisms (Lu and Metcalf 1975), 1,3-dichlorobenzene would be expected to be bioaccumulated by aquatic organisms at least as much as chlorobenzene.

74.4.7 Biotransformation and Biodegradation

According to Ware and West (1977), the more highly halogenated a compound becomes, the more resistant it is to biodegradation. Experimental (Lu and Metcalf 1975) as well as empirical evidence (Leo *et al*. 1971; Chiou *et al*. 1977) has been found indicating that chlorobenzene is a persistent chemical and is not readily biodegraded unless the microorganisms present are already growing on another hydrocarbon source. Furthermore, Alexander and Lustigman (1966) found that the presence of a chlorine atom on the benzene ring retarded the rate of biodegradation. On these bases, 1,3-dichlorobenzene, being more highly chlorinated than chlorobenzene, would presumably biodegrade at least as slowly as chlorobenzene under the same conditions of exposure to microorganisms.

Evidence that 1,3-dichlorobenzene is a persistent chemical is presented in a study by Thom and Agg (1975), which lists 1,3-dichlorobenzene as a synthetic organic chemical which is unlikely to be removed during biological sewage treatment, even after prolonged exposure of the biota. In contrast, Thom and Agg (1975) list chlorobenzene, a compound with one less chlorine atom than 1,3-dichlorobenzene, as a synthetic organic chemical which should be degradable by biological sewage treatment provided that suitable acclimatization can be achieved. Based upon inference 1,3-dichlorobenzene should be resistant to biodegradation but in the absence of solid experimental evidence, no definitive conclusions can be reached or its biodegradability.

74.5 Data Summary

There is not enough environmentally significant information on photolysis, oxidation, sorption, or biodegradation processes to be able to predict the aquatic fate of 1,3-dichlorobenzene. 1,3-Dichlorobenzene has a high affinity for lipophilic materials and is reported to have a relatively low vapor pressure and low solubility at temperatures expected to prevail in most ambient waters. Consequently, sorption, bioaccumulation, and volatilization are expected to be competing processes. The rate at which each of these competing processes occur will dictate which fate is predominant for 1,3-dichlorobenzene in the aquatic environment. These data are summarized in Table 74-1.

Table 74-1

Summary of Aquatic Fate of 1,3-Dichlorobenzene

Environmental Process[a]	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	No information found.	-	-	-
Oxidation	Dichlorobenzenes in general were reported to be reactive toward hydroxyl radicals (OH·) in air.	-	~3 days[b]	Low
Hydrolysis	1,3-Dichlorobenzene will probably not hydrolyze in ambient waters due to the extreme difficulty with which aryl halides undergo nucleophilic substitution.	-	-	Medium
Volatilization	This compound probably volatilizes from the water column to the atmosphere at a relatively rapid rate.	-	~10 or more hours[c]	Medium
Sorption	The high log P value found for 1,3-dichlorobenzene indicates that sorption processes may be substantial for this compound at pollutant concentrations anticipated in environmental waters.	-	-	Medium
Bioaccumulation	Empirical evidence indicates that 1,3-dichlorobenzene will bioaccumulate in the lipids of tissues of living organisms.	-	-	Medium
Biotransformation/ Biodegradation	Will biodegrade, at best, at a very slow rate.	-	-	Low

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. This half-life is the reported half-life of dichlorobenzenes toward hydroxyl radicals in air cited in Ware and West (1977).

c. This half-life is based on the calculated Henry constant of 1,3-dichlorobenzene which is of the same order as the Henry constant predicted for Aroclor 1248 at 25°C by Mackay and Leinonen (1975). Since the half-life for evaporation of Aroclor 1248 from a water column one meter thick was estimated by Mackay and Leinonen to be 9.53 hours at 25°C, the half-life for evaporation of 1,3-dichlorobenzene under the same conditions was assumed to be of the same order, or approximately 10 or more hours.

74.6 Literature Cited

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75. 1,4-DICHLOROBENZENE (p-DICHLOROBENZENE)

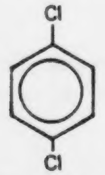
75.1 Statement of Probable Fate

Based on the information found, it is not possible to determine the predominant aquatic fate of 1,4-dichlorobenzene. There is some evidence that dichlorobenzenes in general are reactive toward hydroxyl radicals in air with a half-life of approximately three days. Products and further details of such photooxidation reactions, however, were not indicated. Information concerning the biodegradation potential of 1,4-dichlorobenzene indicates that this compound is very persistent and will probably, at best, be biodegraded very slowly by microorganisms already growing on another hydrocarbon source.

1,4-Dichlorobenzene has a high affinity for lipophilic materials, have a relatively low aqueous solubility and low vapor pressure at ambient temperatures. Consequently, sorption, bioaccumulation, and volatilization are expected to be competing processes. The rate at which each of these competing processes occur will determine which fate is predominant for 1,4-dichlorobenzene in the aquatic environment. Should volatilization occur at a more rapid rate than sorption or bioaccumulation, then atmospheric processes would be expected to regulate the fate of 1,4-dichlorobenzene. On the other hand, should sorption and bioaccumulation occur more rapidly than volatilization, biodegradation of 1,4-dichlorobenzene by aquatic microorganisms would be anticipated to regulate the fate of this compound.

75.2 Identification

1,4-Dichlorobenzene has been detected in drinking water, in superchlorinated municipal wastewaters, in ground water (U.S. Environmental Protection Agency 1975), in wastewater effluent (Glaze and Henderson 1975), and in the atmosphere (Ware and West 1977). The chemical structure of 1,4-dichlorobenzene is shown below.



1,4-Dichlorobenzene

CAS NO. 106-46-7
TSL NO. CZ 45500

Alternate Names

p-Dichlorobenzene
Paradichlorobenzene

75.3 Physical Properties

The general physical properties of 1,4-dichlorobenzene are given below.

Molecular weight (Weast 1977)	147.01
Melting point (Weast 1977)	53.1°C
Boiling point at 760 torr (Weast 1977)	174°C
Vapor pressure at 25°C	*
Solubility in water at 25°C (Verschueren 1977)	79 mg/l
Log octanol/water partition coefficient (Leo *et al*. 1971; Chiou *et al*. 1977)	3.39

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*The value of the vapor pressure of 1,4-dichlorobenzene at 25°C was obtained by interpolation from the values at 20°C (0.6 torr) and 30°C (1.8 torr) from Gray (1957). The value at 25°C was calculated to be 1.18 torr. For further explanation, see Methods section.

75.4 Summary of Fate Data

75.4.1 Photolysis

No specific information pertaining to the direct photolysis of 1,4-dichlorobenzene in the aquatic or atmospheric environments was found.

75.4.2 Oxidation

According to Ware and West (1977) 1,4-dichlorobenzene is resistant to autooxidation by the peroxy radical ($RO_2\cdot$) in water. No more details of this phenomenon were reported.

Dichlorobenzenes in general were reported by Ware and West (1977) to be reactive toward hydroxyl radicals ($OH\cdot$) in air with a half-life of approximately three days. Products and further details of such photooxidation reactions were not indicated. 1,4-Dichlorobenzene, specifically, was reported by Ware and West (1977) to be resistant to autooxidation by ozone in air.

75.4.3 Hydrolysis

No specific information pertaining to the hydrolysis of 1,4-dichlorobenzene has been found. Although Ware and West (1977) report that the inductive electronegative effect of halogen substituents activates the ring making such compounds more easily attacked by nucleophiles such as OH^-, Morrison and Boyd (1973) report that aryl halides are characterized by very low reactivity toward nucleophilic reagents such as OH^-. As an example of the difficulty with which aryl halides undergo nucleophilic substitution, the conditions necessary for the nucleophilic substitution of hexachlorobenzene to a pentachlorophenyl derivative were reported by Patai (1973) to be the presence of aqueous ammonia at a temperature of at least 250°C. On these bases, 1,4-dichlorobenzene, being less chlorinated and, consequently, less easily attacked by nucleophiles than hexachlorobenzene, would not be expected to undergo hydrolysis at an appreciable rate under environmental conditions.

75.4.4 Volatilization

Available data on 1,4-dichlorobenzene indicate that this compound probably volatilizes from the water column to the atmosphere at a relatively rapid rate. Garrison and Hill (1972) reported that a 300 mg/l concentration of 1,4-dichlorobenzene volatilized almost completely (less than 1 mg/l of 1,4-dichlorobenzene remained) from aerated distilled water in less than 4 hours. The same concentration of 1,4-dichlorobenzene revolatilized almost completely (less than 1 mg/l of 1,4-dichlorobenzene remained) from unaerated distilled water in less than 3 days. No further details of this experiment were reported. The data of Garrison and Hill (1972) can be used to calculate approximate values for evaporative half-lives. For the aerated solution, the calculated half-life is less than 30 minutes; however, since the aeration probably caused air-stripping of the 1,4-dichlorobenzene, this value is not recommended as an evaporative half-life under conditions of agitation. The data for unaerated conditions, apparently close to quiescence, correspond to a half-life of less than about nine hours.

According to Mackay and Wolkoff (1973) the rate of evaporation of pollutants having a low solubility in water can be quite rapid even though these compounds often have a high molecular weight and a low vapor pressure, and should, on these bases, evaporate slowly. Mackay and Wolkoff (1973) contend that these compounds often have high activity coefficients in water which cause unexpectedly high equilibrium partial vapor pressures and thus high rates of evaporation. Although 1,4-dichlorobenzene, which has a moderately low vapor pressure (1.18 torr) and a low solubility in water of 79 mg/l at 25°C (Verschueren 1977) was not mentioned specifically, other chlorinated hydrocarbons having a low solubility in water were predicted to have relatively rapid rates of evaporation. Presumably, 1,4-

dichlorobenzene would have a rate of evaporation similar to those chlorinated compounds having vapor pressure and solubility values approximately equal to those values for 1,4-dichlorobenzene.

The calculated value for the vapor pressure (Gray 1957) and published value for the solubility in water (Verschueren 1977) of 1,4-dichlorobenzene were used to compute the Henry constant as being approximately 2.88 x 10^{-3} atmos. m^3/mole which may be compared to the value of 2.76 x 10^{-3} atmos. m^3/mole predicted for Aroclor 1254 at 25°C (Mackay and Leinonen 1975). In the case of Aroclor 1254, the half-life for evaporation from a water column one meter thick was estimated by Mackay and Leinonen (1975) to be 10.3 hours at 25°C. An estimate of the corresponding half-life for evaporation of 1,4-dichlorobenzene under the same conditions would presumably be of the same order, approximately 11 or more hours. Mackay and Leinonen (1975) point out that interpretation of the environmental significance of the rate of evaporation of compounds such as 1,4-dichlorobenzene from environmental waters using values calculated at 1 meter depth is dependent upon the type of environmental situation encountered. In situations where the water body is turbulent with frequent mixing between the surface layer and the bulk, as in a rapidly flowing shallow river or during white-capping on a lake or ocean, the rate of evaporation would be more rapid than for depths greater than 1 meter or in quiescent water, as exists in a deep, slowly flowing river.

75.4.5 Sorption

Although no specific environmental sorption studies were found in the literature, the value of the log octanol/water partition coefficient for 1,4-dichlorobenzene (log P = 3.39, Leo *et al.* 1971) indicates that sorption processes may be substantial for 1,4-dichlorobenzene at pollutant concentrations anticipated in environmental waters. Presumably, 1,4-dichlorobenzene will be adsorbed by sedimentary organic material; the extent to which this possible adsorption will interfere with volatilization has not been considered.

75.4.6 Bioaccumulation

Although no experimental evidence of the bioaccumulation potential of 1,4-dichlorobenzene was found, there is empirical evidence that 1,4-dichlorobenzene has a high potential for bioaccumulation in aquatic organisms. Neely *et al.* (1974) and Lu and Metcalf (1975) have shown that the log octanol/water partition coefficient (log P) correlates well with the ability of a compound to accumulate in the lipids of tissues of living organisms. Furthermore, the incorporation of chlorine into an organic molecule increases its lipophilic character resulting in an increased bioaccumulation potential (Kopperman *et al.* 1976). For comparison, chlorobenzene, a compound containing only one chlorine atom, and 1,4-dichlorobenzene, a compound having two chlorine atoms, have log P values of 2.84 (Leo et al. 1971; Chiou et al. 1977) and 3.39 (Leo et al. 1971), respectively. Since it has been established experimentally that chlorobenzene bioaccumulates in aquatic organisms (Lu and Metcalf 1975), 1,4-dichlorobenzene, would be expected to be bioaccumulated by aquatic organisms at least as much as chlorobenzene.

75.4.7 Biotransformation and Biodegradation

According to Ware and West (1977), the more highly halogenated a compound becomes, the more resistant it is to biodegradation. Experimental (Lu and Metcalf 1975) as well as empirical evidence (Leo et al. 1971; Chiou et al. 1977) has been found indicating that chlorobenzene is a persistent chemical and is not readily biodegraded unless the microorganisms present are already growing on another hydrocarbon source. Furthermore, Alexander and Lustigman (1966) found that the presence of a chlorine atom on the benzene ring retarded the rate of biodegradation. On these bases, 1,4-dichlorobenzene, being more highly chlorinated than chlorobenzene, would presumably biodegrade at least as slowly as chlorobenzene under the same conditions of exposure to microorganisms.

Evidence that 1,4-dichlorobenzene is a persistent chemical is presented in a study by Thom and Agg (1975) which lists 1,4-dichlorobenzene as a synthetic organic chemical which is unlikely to be removed during biological sewage treatment, even after prolonged exposure of the biota. In contrast, Thom and Agg (1975) list chlorobenzene, a compound with one less chlorine atom than 1,4-dichlorobenzene, as a synthetic organic chemical which should be degradable by biological sewage treatment provided that suitable acclimatization can be achieved. Based upon inference 1,4-dichlorobenzene should be resistant to biodegradation but in the absence of solid experimental evidence no definite conclusions can be reached on its biodegradability.

75.5 Data Summary

There is not enough environmentally significant information on photolysis, oxidation, sorption, or biodegradation processes to be able to predict the fate of 1,4-dichlorobenzene. 1,4-Dichlorobenzene has a high affinity for lipophilic materials, yet it is reported to have a relatively low vapor pressure and low solubility at temperatures expected to prevail in most ambient waters. Consequently, sorption, bioaccumulation, and volatilization are expected to be competing processes. The rate at which each of these competing processes occur will dictate which fate is predominant for 1,4-dichlorobenzene in the aquatic environment. These data are summarized in Table 75-1.

Table 75-1

Summary of Aquatic Fate of 1,4-Dichlorobenzene

Environmental Process[a]	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	No information found.	-	-	-
Oxidation	1,4-Dichlorobenzene is reported to be resistant to autooxidation by the peroxy radical ($Ro_2\cdot$) in water. Dichlorobenzenes were reported to be reactive toward hydroxyl radicals ($OH\cdot$) in air.	-	~3 days[b]	Low
Hydrolysis	1,4-Dichlorobenzene will probably not hydrolyze in ambient waters due to the extreme difficulty with which aryl halides undergo nucleophilic substitution.	-	-	Medium
Volatilization	This compound probably volatilizes from the water column to the atmosphere at a relatively rapid rate.	-	11 or 12 hours[c] < 9 hours[d]	Medium
Sorption	The high log P value found for 1,4-dichlorobenzene indicates that sorption processes may be substantial for this compound at pollutant concentrations anticipated in environmental waters.	-	-	Medium
Bioaccumulation	Empirical evidence indicates that 1,4-dichlorobenzene will bioaccumulate in the lipids of tissues of living organisms.	-	-	Low
Biotransformation/ Biodegradation	Will biodgrade, at best, at a very slow rate.	-	-	Low

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. This half-life is the reported half-life of dichlorobenzenes toward hydroxyl radicals in air cited in Ware and West (1977).

c. This half-life is based on the calculated Henry constant of 1,4-dichlorobenzene which is of the same order as the Henry constant predicted for Aroclor 1254 at 25°C by Mackay and Leinonen (1975). Since the half-life for evaporation of Aroclor 1254 from a water column one meter thick was estimated by Mackay and Leinonen to be 10.3 hours at 25°C, the half-life for evaporation of 1,4-dichlorobenzene under the same conditions was assumed to be of the same order; at most, 11 or 12 hours.

d. This half-life is the estimated half-life based on the experimental results and conditions of Garrison and Hill (1972) in unaerated distilled water.

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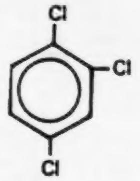
76. 1,2,4-TRICHLOROBENZENE

76.1 Statement of Probable Fate

1,2,4-Trichlorobenzene has a high affinity for lipophilic materials and is reported to exhibit a relatively high rate of volatilization from aqueous systems. Consequently, sorption, bioaccumulation, and volatilization are anticipated to be competing processes. The rates at which these competing processes occur will determine which fate is predominant for 1,2,4-trichlorobenzene in the aquatic environment, but the data found were insufficient to determine the most rapid process. Should volatilization occur at a more rapid rate than sorption or bioaccumulation, then atmospheric processes would be expected to regulate the fate of 1,2,4-trichlorobenzene. On the other hand, should sorption and bioaccumulation occur more rapidly than volatilization, biodegradation of 1,2,4-trichlorobenzene by aquatic microorganisms would be anticipated to regulate the fate of this compound.

76.2 Identification

1,2,4-Trichlorobenzene has been detected in drinking water (U.S. Environmental Protection Agency 1975), in wastewater effluent (Glaze and Henderson 1975), and in the atmosphere (Ware and West 1977). The chemical structure of 1,2,4-trichlorobenzene is shown below.



1,2,4-Trichlorobenzene

Alternate Name

unsym-Trichlorobenzene

CAS NO. 120-82-1
TSL NO. DC 21000

76.3 Physical Properties

The general physical properties of 1,2,4-trichlorobenzene are as follows.

Molecular weight (Weast 1977)	181.45
Melting point (Weast 1977)	16.95°C

Boiling point at 760 torr (Weast 1977)	213.5°C
Vapor pressure at 25°C	0.42 torr (calculated)
Solubility in water at 25°C (Dow 1978)	30 mg/l
Log octanol/water partition coefficient (Calculated from Tute 1971; See Methods section on Bioaccumulation)	4.26

76.4 Summary of Fate Data

76.4.1 Photolysis

No specific information pertaining to the direct photolysis of 1,2,4-trichlorobenzene in the aquatic or atmospheric environments was found.

76.4.2 Oxidation

No specific information pertaining to the oxidation of 1,2,4-trichlorobenzene in the aquatic environment was found. 1,2,4-Trichlorobenzene, however, was reported by Simmons et al. (1976) to be susceptible to attack by hydroxyl radicals in the atmosphere. The rate of this reaction is not known, but the half-life was estimated by Simmons et al. (1976) to be one to several days.

76.4.3 Hydrolysis

No specific information pertaining to the hydrolysis of 1,2,4-trichlorobenzene in ambient waters was found. Although Ware and West (1977) report that the inductive electronegative effect of halogen substitutents activates the ring making such compounds more easily attacked by nucleophiles such as OH^-, Morrison and Boyd (1973) report that aryl halides will undergo nucleophilic substitution only with extreme difficulty. For example, Patai (1973) reported that the minimum conditions necessary for the nucleophilic subtitution of hexachlorobenzene to a pentachlorophenyl derivative were the presence of aqueous ammonia and a temperature of 250°C. On these bases, 1,2,4-trichlorobenzene, being less chlorinated and, consequently, less easily attacked by nucleophiles than hexachlorobenzene, would not be expected to undergo hydrolysis at an appreciable rate under environmental conditions.

76.4.4 Volatilization

Available data on 1,2,4-trichlorobenzene indicate that this compound probably volatilizes from the water column to the atmosphere at a relatively rapid rate. Ware and West (1977) cited information in which the half-life for evaporation of 1,2,4-trichlorobenzene from water is 45 minutes at standard temperature and pressure. Garrison and Hill (1972) reported that at 100 mg/l 1,2,4-trichlorobenzene volatilized almost completely (less than 1 mg/l of 1,2,4-trichlorobenzene remained) from aerated distilled water in less than 4 hours. The same concentration of 1,2,4-trichlorobenzene volatilized almost completely (less than 1 mg/l of 1,2,4-trichlorobenzene remained) from unaerated distilled water in less than 2 days. No further details of this experiment were reported.

Assuming that volatilization as reported by Garrison and Hill (1972) is a first order process, then the evaporative half-lives corresponding to the above data are 36 minutes for the aerated condition and 7.2 hours for the unaerated (quiescent) condition. The evaporation half-life of 45 minutes cited by Ware and West (1977) is very close to the 36 minutes resulting from aeration; aeration is assumed to have involved some gas stripping of the 1,2,4-trichlorobenzene from the solution.

In a separate experiment by Garrison and Hill (1972) an aqueous solution of 1,2,4-trichlorobenzene (50 mg/l) was exposed to mixed cultures of aerobic microorganisms and aerated. Based on the graphical representation of the data by Garrison and Hill (1972) and assuming a negligible rate of biodegradation in comparison to volatilization (no degradation products were found), the evaporative half-life for the 1,2,4-trichlorobenzene in this system appears to be on the order of 4 to 5 hours. A measurable concentration of the compound was detected after nine days of exposure. In this experiment, the half-life with respect to volatilization is reasonably close to the 7.2 hours cited above for the quiescent condition in distilled water. It is believed that this result illustrates the effect of partitioning of 1,2,4-trichlorobenzene between the water and suspended biological material.

In summary, the rate of volatilization of 1,2,4-trichlorobenzene from distilled water is relatively high, but, when suspended organic materials are present, the partitioning between water and suspended solids can greatly reduce the volatilization rate.

76.4.5 Sorption

Although no specific environmental sorption studies were found in the literature, the calculated value of the log octanol/water partition coefficient found for 1,2,4-trichlorobenzene (log P = 4.26, Tute 1971) indicates that sorption processes may be substantial for this compound at pollutant concentrations anticipated in environmental waters. Presumably, 1,2,4-trichlorobenzene will be adsorbed by sedimentary organic material; the extent to which this possible adsorption will interfere with volatilization has not been studied.

76.4.6 Bioaccumulation

Macek et al. (1977) investigated the relative significance of aqueous and dietary exposure of bluegill sunfish (Lepomis macrochirus) to 1,2,4-trichlorobenzene using an aquatic food chain which consisted of a food organism, the water flea, Daphnia magna, and a consumer organism, the bluegill sunfish, Lepomis macrochirus. Prior to initiation of the food chain experiment, the duration of exposure required to "load" daphnids and fish to an equilibrium concentration of radiolabelled 1,2,4-trichlorobenzene was determined. Two flow-through experimental units (A,B) were dosed to maintain continuous aqueous exposure of bluegill sunfish to a concentration of 3.0 µg/l of 1,2,4-trichlorobenzene. Two other flow-through experimental units (C,D) contained no aqueous concentrations of 1,2,4-trichlorobenzene. Fish in units B and C were fed daphnids allowed to reach equilibrium concentrations of 1,2,4-trichlorobenzene, while fish in A and D were fed uncontaminated daphnids. As a result, fish in unit A experienced only aqueous exposure to the chemical, fish in unit B experienced both dietary and aqueous exposure, fish in unit C experienced only dietary exposure, and fish in unit D experienced no exposure and served as a control group. Quantitative measures of the accumulation of ^{14}C-residues of 1,2,4-trichlorobenzene in bluegill sunfish were determined by removing five fish from each experimental unit on day 1,3,7,10,14 and each succeeding 7 days during exposure and radiometrically analyzing each individual fish.

Daphnids continuously exposed to a mean measured aqueous concentration of 3.1 ± 0.4 µg/l of 1,2,4-trichlorobenzene had a mean measured equilibrium 14-C residue body burden of 0.44 ± 0.16 mg/l. Therefore, the estimated equilibrium bioconcentration factor for daphnids is 142X. Fish continuously exposed to a mean measured aqueous concentration of 2.9 ± 1.1 µg/l of 1,2,4-trichlorobenzene had a mean measured equilibrium 14-C residue body burden of 0.53 + 0.25 mg/l. Consequently, the estimated equilibrium bioconcentration factor for fish is 182X. Macek et al. (1977) define bioconcentration as that process whereby chemical substances enter aquatic organisms through gills or epithelial tissues directly from water. Bioaccumulation, on the other hand, is defined by Macek et al. (1977) as a broader term referring to a process which includes bioconcentration as well as any uptake of chemical residues from dietary sources. The data from investigating the bioaccumulation of 14-C 1,2,4-trichlorobenzene by bluegill sunfish from food and water yielded a mean equilibrium 14-C residue body burden in sunfish of 0.57 ± 0.5 mg/l when exposed to 2.9 µg/l of 1,2,4-trichlorobenzene and fed daphnids having a mean concentration of 0.44 mg/l of 14-C residue.

The drawback of the experiments of Macek et al. 1977 is that either results are based upon total c^{14}-carbon analysis and hence do not take into account metabolic by-products and bound residues. If biodegradation does not occur, their bioconcentration factors will be maximal. Under the conditions of the experiment, however, bioconcentration factors very likely will be lower.

Macek et al. (1977) concluded that the contribution of the dietary source of 1,2,4-trichlorobenzene to the ultimate equilibrium body burden is probably insignificant compared to the aqueous source of this chemical even if the two sources are additive. The lack of significant contribution of dietary 1,2,4-trichlorobenzene to the equilibrium 14-C residue body burden of bluegill sunfish was confirmed by results of a study where bluegill sunfish were held in uncontaminated water but fed daphnids containing 0.44 mg/l of 14-C residues as 1,2,4-trichlorobenzene. The mean 14-C residue body burden in bluegill sunfish during dietary exposure to approximately 3 µg/l of 1,2,4-trichlorobenzene was 0.03 ± 0.01 mg/l. This value represents only about 5 percent of the 1,2,4-trichlorobenzene 14-C residue body burden in bluegill sunfish exposed for a comparable period to either aqueous or combined aqueous and dietary 1,2,4-trichlorobenzene. Macek et al. (1977) conclude that the percent of residue burden due to dietary intake alone of 1,2,4-trichlorobenzene by bluegill sunfish fed contaminated daphnids is less than the error associated with the ability to estimate residues due to bioconcentration alone.

Neely et al. (1974) and Lu and Metcalf (1975) have shown that the log octanol/water partition coefficient (log P) correlates well with the ability of a compound to accumulate in the lipids of tissues of living organisms. Furthermore, the incorporation of chlorine into an organic molecule increases its lipophilic character resulting in an increased potential for bioaccumulation (Kopperman et al. 1976). The rather high log P value of 4.26 as calculated from the method of Tute (1971) indicates that the bioaccumulation potential of 1,2,4-trichlorobenzene by aquatic organisms at pollutant concentrations anticipated in environmental waters would probably be relatively high. Based upon the minimal available evidence, however, 1,2,4-trichlorobenzene appears not to be bioaccumulated as extensively as chlorobenzene. Whether this is a function of insufficient sampling or an exception to the connection between log P and bioaccumulation cannot yet be determined.

76.4.7 Biotransformation and Biodegradation

Experimental evidence indicates that chlorobenzene, which is structurally similar to 1,2,4-trichlorobenzene but less highly chlorinated, is not readily biodegraded unless the microorganisms present are already utilizing another carbon source (Gibson et al. 1968). According to Ware and West (1977), resistance to biodegradation generally increases as the degree of halogenation of a compound increases, and Alexander and Lustigman (1966) found that the presence of a chlorine atom on the benzene ring retarded the rate of biodegradation. From the above, it can be inferred that 1,2,4-trichlorobenzene, being more highly chlorinated than chlorobenzene, would presumably be biodegraded less rapidly than chlorobenzene under the same conditions of exposure to microorganisms.

Ware and West (1977) report an experiment in which 1,2,4-trichlorobenzene at a concentration of 50 mg/l was exposed to preconditioned treatment plant cultures. 1,2,4-Trichlorobenzene was very persistent as evidenced by the slight decrease in concentration probably due primarily to atmospheric loss after a 50-hour period. The microorganisms absorbed approximately 40 percent of 1,2,4-trichlorobenzene but did not substantially biodegrade the absorbed portion.

Ware and West (1977) also report another experiment in which the biodegradation of 1,2,4-trichlorobenzene was studied in order to assess the extent and rate of degradation and the role of acclimatization. When unacclimatized industrial wastewater microorganisms were used, 99 percent of the 1,2,4-trichlorobenzene at an initial concentration of 1.7 mg/l disappeared from the experimental mixture after 10 days. The BOD (Biochemical Oxygen Demand) value after 10 days, however, indicated that only 55 percent of the theoretical value was removed. The 45 percent theoretical oxygen demand remaining was assumed to be due to incompletely oxidized metabolites of 1,2,4-trichlorobenzene which were probably incorporated in the cell wall. The experiments found no apparent degradation as measured by BOD in the first few days of monitoring. Analysis, however, indicated a 14 percent reduction in the concentration of 1,2,4-trichlorobenzene after 24 hours, a 36 percent reduction at 72 hours, and a 43 percent reduction at 7 days. At a concentration of 2.6 mg/l the rate of degradation was apparently lower for the first few days. After seven days of exposure of the microorganisms to a concentration of 2.6 mg/l of 1,2,4-trichlorobenzene, analysis indicated 28 percent decrease in the concentration of 1,2,4-trichlorobenzene. This is quite different from the 43 percent decrease of 1,2,4-trichlorobenzene after seven days of exposure of the microorganisms to a concentration of 1.7 mg/l of this compound. After ten days, however, all of the 1,2,4-trichlorobenzene at the higher concentration had disappeared from the BOD bottles.

Ware and West (1977) reported another phase of the previous experiment in which the formation rate of carbon-14 labeled CO_2 through biodegradation of 1,2,4-trichlorobenzene by activated sludge was examined. After 5 days, 13 percent of the 1,2,4-trichlorobenzene remained, while 56 percent was converted to carbon dioxide, 23 percent to polar metabolites, and 7 percent was volatilized. Approximately 80 percent of the 1,2,4-trichlorobenzene was adsorbed on solids, accounting for the low volatility from the system. In summary, biodegradation of 1,2,4-trichlorobenzene has been demonstrated under conditions where microorganisms are acclimated and another carbon source is utilized, as in the activated sludge process. Under environmental conditions, biodegradation would be expected but at a very much lower rate than in the waste treatment studies reported above.

76.5 Data Summary

Information found concerning photolysis, oxidation, or sorption processes was insufficient to allow prediction of the aquatic fate of 1,2,4-trichlorobenzene. 1,2,4-Trichlorobenzene has a high affinity for lipophilic materials and is predicted to have a relatively low vapor pressure and low solubility at ambient temperatures. Consequently, sorption and bioaccumulation are expected to be competing with volatilization in removing the compound from the water column. The rate at which each of these competing processes occur will dictate which fate is predominant for 1,2,4-trichlorobenzene in ambient waters. These data are summarized in Table 76-1.

Table 76-1

Summary of Aquatic Fate of 1,2,4-Trichlorobenzene

Environmental Process[a]	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	No information found.	-	-	-
Oxidation	1,2,4-Trichlorobenzene is reported to be susceptible to attack by hydroxyl radicals in the atmosphere.		one to several days[b]	Low
Hydrolysis	1,2,4-Trichlorobenzene will probably not hydrolyze in ambient water due to the extreme difficulty with which aryl halides undergo nucleophilic substitution.	-	-	Medium
Volatilization	This compound probably volatilizes from the water column to the atmosphere at a relatively rapid rate.		∿45 minutes[c]	Medium
Sorption	The high log P value found for 1,2,4-trichlorobenzene indicates that sorption processes may be substantial for this compound in environmental waters.	-	-	Low
Bioaccumulation	Empirical evidence indicates that 1,2,4-trichlorobenzene has a high potential for bioaccumulation in the lipids of tissues of living organisms.	-	-	Medium
Biotransformation/ Biodegradation	Will biodegrade, at best, at a very slow rate.	-	-	Medium

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. This is the estimated half-life for 1,2,4-trichlorobenzene reacting with hydroxyl radicals in air (Simmons *et al*. 1976).

c. This value is the half-life calculated for the evaporation of 1,2,4-trichlorobenzene from water 10 cm deep measured at standard temperature and pressure as cited in Ware and West (1977).

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77. HEXACHLOROBENZENE

77.1 Statement of Probable Fate

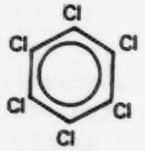
Based on the information found, it appears that hexachlorobenzene is a very persistent compound. None of the destructive processes studied, which include photolysis, oxidation, hydrolysis, and biodegradation, appear to exert an appreciable effect on the fate of hexachlorobenzene in the aquatic environment. Some investigators believe that naturally occurring complex organic compounds present in rivers and streams may serve as photosensitizers and thus enhance the degradation of organic pollutants, such as hexachlorobenzene, by sunlight. The photolysis of hexachlorobenzene in the presence of such possible photosensitizers, however, has not been studied. The relative volatility of hexachlorobenzene is not known. Should hexachlorobenzene prove to be volatile and enter into the upper atmosphere, there is a possibility that short wavelength light may eventually convert this pollutant into other compounds. No evidence that this does occur, however, has been found.

Hexachlorobenzene has a high affinity for lipophilic materials. Consequently, sorption and bioaccumulation are anticipated to occur quite readily. It appears that the majority of hexachlorobenzene found in aquatic organisms is from aqueous rather than dietary sources. Furthermore, rates of depuration of hexachlorobenzene from exposed aquatic organisms are substantially more rapid than rates of depuration reported for such highly persistent compounds as DDT. Therefore, biomagnification of hexachlorobenzene through aquatic food chains probably does not occur.

77.2 Identification

Hexachlorobenzene has been found in water and sediment samples, and in aquatic biota from a known site of contamination in the lower Mississippi River (Laseter *et al*. 1976; Laska *et al*. 1976), in many species of fish collected throughout the United States (Johnson *et al*. 1974), in drinking water supplies and finished drinking water of several cities in the United States (U.S. Environmental Protection Agency 1975), in food products and in samples of human fatty tissue from individuals in the population of Italy (Leoni and D'Arca 1976), and as an impurity in several agricultural pesticides (Leoni and D'Arca 1976).

The chemical structure of hexachlorobenzene is shown below.



	Alternate Names
Hexachlorobenzene	Perchlorobenzene HCB

CAS NO. 118-74-1
TSL NO. DA 29750

77.3 Physical Properties

The general physical properties of hexachlorobenzene are given below.

Molecular weight (Weast 1977)	284.79
Melting point (Weast 1977)	230°C
Boiling point (Weast 1977)	322°C
Vapor pressure at 20°C (Leoni and D'Arca 1976; Isenee *et al.* 1976)	1.089×10^{-5} torr
Solubility in water	*
Log octanol/water partition coefficient (Neely *et al.* 1974)	6.18

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*According to Laseter *et al.* (1976) the upper limit of solubility of hexachlorobenzene in water is 20 μg/l. Although no temperature or pH was given at which this upper limit of solubility was determined, it is assumed that these parameters would be within the limits found in environmental waters. Metcalf *et al.* (1973) measured the solubility of HCB at 25°C by radioassay and obtained a value of 6 μg/l.

77.4 Summary of Fate Data

77.4.1 Photolysis

Plimmer and Klingebiel (1976) investigated photodecomposition as a possible route for the environmental degradation of hexachlorobenzene. In one experiment, a layer of crystalline hexachlorobenzene was placed on a glass plate under a quartz cover and exposed for five months to a sunlamp or to ambient laboratory illumination. In another experiment, a hexane solution of hexachlorobenzene was spotted on silica gel coated thin layer chromatography plates which were subsequently exposed for 4.5 hours to outdoor sunlight, to a 40-W sunlamp (maximum wavelength about 310 nm), or to laboratory illumination (fluorescent lighting). These experiments indicated that photodecomposition of hexachlorobenzene was extremely slow. No photodecomposition products were identified. According to Plimmer and Klingebiel (1976), this photodecomposition is unlikely to be sensitized by triplet-state energy transfer since two triplet sensitizers of similar triplet state energies, diphenylamine and benzophenone, did and did not sensitize hexachlorobenzene photolysis, respectively. It was suggested that other related amines might function in a manner analogous to diphenylamine through a charge-transfer mechanism. From these studies, Plimmer and Klingebiel (1976) conclude that photodecomposition of hexachlorobenzene in the solid state is expected to be slow. They indicate, however, that complex naturally occurring organic compounds present in rivers and streams (such as humic acids) may serve as photosensitizers and thus enhance the degradation of organic pollutants by sunlight. The photolysis of hexachlorobenzene in the presence of such possible photosensitizers has not been studied.

Laseter et al. (1976) exposed solutions of hexachlorobenzene in both hexane and benzene to irradiation for periods of 30, 65, and 120 minutes. The "Laboratory Methods and Materials" section of their report states that irradiations were conducted at a wavelength of 253.7 nm in capped quartz test tubes, but the "Results" section of the paper states that irradiations were conducted at a wavelength of 273.5 nm. Less than 10 percent of the original hexachlorobenzene was reported to remain after 60 minutes of irradiation in benzene. Concurrently, a gradual increase of lower molecular weight products commenced after 30 minutes of irradiation. Based on the fact that both of the aforementioned wavelengths are below the atmospheric cutoff, it appears that direct photolysis would probably not be an important fate process for hexachlorobenzene in the aquatic environment.

77.4.2 Oxidation

The stability of hexachlorobenzene is such that it is resistant to oxidation except under the most extreme conditions (Fieser and Fieser 1956). Consequently, oxidation of hexachlorobenzene would not be expected to be an important fate under ambient conditions.

77.4.3 Hydrolysis

Although Ware and West (1977) report that the electronegative effect of aromatic halogen substituents activates the benzene ring and renders it more easily attacked by nucleophiles such as OH^-, Morrison and Boyd (1973) report that aryl halides will undergo nucleophilic substitution only with extreme difficulty. For example, Patai (1973) reported that the minimum conditions necessary for the nucleophilic substitution of hexachlorobenzene to a pentachlorophenyl derivative were the presence of aqueous ammonia and a temperature of 250°C. Furthermore, Leoni and D'Arca (1976) report that hexachlorobenzene is chemically very inert at room temperature and reacts with caustic alkalis to form the corresponding pentachlorophenolates only at 130°-200°C. Thus, hexachlorobenzene would not be expected to undergo hydrolysis at an appreciable rate under environmental conditions.

77.4.4 Volatilization

Because of its relatively high boiling point and correspondingly low vapor pressure at ambient temperature, hexachlorobenzene might be expected to exhibit very slow rates of volatilization from water. Mackay and Wolkoff (1973), however, contend that sparingly soluble organic compounds often have high activity coefficients in aqueous solution which cause unexpectedly high equilibrium partial vapor pressures and high rates of evaporation. Hexachlorobenzene, with an aqueous solubility on the order of 10 μg/l (Laseter *et al*. 1976; Metcalf *et al*. 1973) may be such a compound, but experimental information on this point was not found. Calculations according to Mackay and Leinonen (1975) predict a rate constant of 0.08/min or a $t_{1/2}$ of ~ 8 hours for evaporation from a water column 1 m deep. Although such an estimate does not include environmentally important parameters such as adsorption by sediment and variable mixing rates, it does suggest that transport by volatilization might be important in the absence of other processes.

77.4.5 Sorption

Laseter *et al*. (1976) conducted an experiment in which a soil sample was exposed to a regular flow of water with a concentration of 8.3 μg/l hexachlorobenzene. After one day of exposure to this concentration, the soil sample had a concentration of 332 μg/l of hexachlorobenzene, a concentration factor of 40X. Four days after initiation of the test, the concentration of hexachlorobenzene in the soil was 269 μg/l, a concentration factor of 32X. Depuration was initiated on the fourth day of exposure, and after four days of depuration the sample of sediment had a concentration of 303 μg/l of hexachlorobenzene, a concentration almost as high as that measured on the first day of exposure. Laseter *et al*. (1976) concluded that bottom sediment accumulated proportionately less hexachlorobenzene than did organisms, but retained it longer.

Laska *et al*. (1976) studied the distribution of hexachlorobenzene in the vicinity of an industrialized region bordering the Mississippi River between Baton Rouge and New Orleans, Louisiana. The mean concentration of hexachlorobenzene in water from the Mississippi River near Baton Bouge was 2.2 µg/l as compared to a concentration of 167.0 µg/l (dry weight) in the soil of the levee adjacent to the river. Laska et al. (1976) attributed the high levels of hexachlorobenzene in the soil on the river side of the levee to accumulation of hexachlorobenzene from the load carried in solution and suspension in river water.

77.4.6 Bioaccumulation

The bioaccumulation potential of hexachlorobenzene has been studied using radiotracer techniques in three model aquatic ecosystems (Metcalf et al. 1973; Lu and Melcalf 1975; Isensee et al. 1976). Descriptions and pertinent results for all three ecosystems are presented below. In all studies, hexachlorobenzene was found to be a highly persistent compound as demonstrated by the ecological magnification values (EM) and bioaccumulation ratios (BR; equivalent to EM).

Metcalf et al. (1973) and Lu and Metcalf (1975) define ecological magnification as the ratio of the parent compound in an organism to the concentration in the water; the term bioaccumulation ratio used by Isensee et al. (1976) has the same meaning as ecological magnification. From this definition and from the three experimental designs, it is unclear as to whether ecological magnification and bioaccumulation ratio are measures of bioconcentration or measures of bioaccumulation. According to Macek et al. (1977), bioconcentration is defined as that process whereby chemical substances enter aquatic organisms through gills or epithelial tissue directly from water. Bioaccumulation, on the other hand, is defined by Macek et al. (1977) as a broader term referring to a process which includes bioconcentration as well as any uptake of chemical residues from dietary souces.

Since the relative contributions of aqueous and dietary sources of hexachlorobenzene were not quantitatively evaluated at equilibrium conditions, it is not possible to determine whether ecological magnification and bioaccumulation ratio are measures of bioaccumulation or bioconcentration. It is, in fact, very possible that the body burden due to dietary and aqueous exposure of hexachlorobenzene would be statistically indistinguishable from the body burden due to aqueous exposure alone of hexachlorobenzene. In a critical analysis of selected chemicals by Macek et al. (1977) which included Kepone, PCB's, endrin, cadmium, DDT, and 1,2,4-trichlorobenzene, the equilibrium body burden due to dietary exposure of these chemicals was statistically indistinguishable from the equilibrium body burden due to aqueous exposure except in the case of DDT.

Reported values of ecological magnification or bioaccumulation ratio for the various species studied in each model ecosystem are presented in Table 77-1. As can be seen, the agreement between results for a given species varies from poor to excellent; in general, the ratios reported by Metcalf et al. (1973) were somewhat lower than those from the other two sets of studies, but the reason for the variation is unclear.

Table 77-1. Values for Ecological Magnification and Bioaccumulation Ratio of Hexachlorobenzene in Three Model Aquatic Ecosystems

Reference	HCB in H_2O Conc. (in ppb)	Values for Ecological Magnification and Bioaccumulation Ratio						
		Oedogonium cardiacum (alga)	Daphnia magna (water flea)	Helisoma sp. (snail)	Physa sp. (snail)	Culex quinquifasciatus (mosquito larva)	Tambusia affinis (mosquito fish)	Ictalurus punctatus (fingerling channel catfish)
Lu and Metcalf (1975)	9.34	3969	1129	-	2672	2622	1166	-
Metcalf *et al.* (1973)	2.98	522	200	-	1248	143	287	-
Isensee *et al.* (1976)	0.03	610	1030	1360	-	-	1260	6160
	0.22	710	770	1510	-	-	1530	9830
	1.72	910	940	1630	-	-	2040	15850

The model aquatic ecosystem of Lu and Metcalf (1975) was devised for studying relatively volatile organic compounds and simulating direct discharge of chemical wastes. A 3-liter flask which contained members of an aquatic food chain, including daphnia, mosquito larvae, snails, mosquito fish, and green filamentous algae, was maintained at 80°F with 12 hours daylight exposure. Radiolabeled pollutants were added to the flask in concentrations of 0.01 to 0.1 mg/l. After 48 hours, the experiment was terminated and samples were taken and analyzed. The data for hexachlorobenzene are shown in Table 77-1.

From a different set of experiments Metcalf *et al*. (1973) estimated the comparative environmental properties of DDT, methoxyclor, and other DDT analogs including hexachlorobenzene. A small glass aquarium that had a sloping terrestrial-aquatic interface of pure sand was used to carry out the aquatic model ecosystem evaluation. A 5-mg portion (equivalent to 1.1 kg/hc) of radiolabeled pesticide was applied to sorghum seedlings grown on the terrestrial portion after which fourth instar salt marsh caterpillars were fed on the leaves until these were consumed. Thus, the fecal products of the larvae and the larvae themselves contaminated the aquatic portion of the system. The radiolabeled products were transferred through several trophic levels in the aquatic food chain, e.g., alga (*Oedogonium cardiacum*) → snail (*Physa*); plankton → water flea (*Daphnia magna*) → mosquito (*Culex pipiens*) → fish (*Gambusia affinis*). After 33 days in this environmental plant growth chamber at 80°F with a 12-hour photoperiod, the experiment was terminated and samples taken and analyzed, with the results for hexachlorobenzene as shown on Table 77-1.

Isenee *et al*. (1976) developed their model aquatic ecosystem specifically to determine the bioaccumulation potential of hexachlorobenzene. In this study, three replicates each of control soil and soils treated with hexachlorobenzene at concentrations of 0.1, 1, and 10 mg/l were placed in tanks to which was added aqueous solutions with concentrations of 0, 10, 100, and 1000 µg/l of hexachlorobenzene, respectively. Twenty-four hours later, approximately 100 daphnids (*Daphnia magna*), eight snails (*Helisoma* sp.), a few strands of an alga (*Oedogonium cardiacum*), and 10 ml of old aquarium water which contained various diatoms, protozoa, and rotifers were added. Water lost by evaporation was replenished as needed. At 30 days, daphnids were sampled for analysis (20 to 30 mixed age organisms per sample) and two 0.15 - 0.25g mosquito fish (*Gambusia affinis*) were added. Three days later all organisms were harvested and two 2.0 - 2.5g fingerling channel catfish (*Ictalurus punctatus*) were added to each tank and exposed for 8 days.

Based on their results, Isensee *et al*. (1976) concluded that hexachlorobenzene is very persistent in aquatic systems. They also found that the amounts of hexachlorobenzene accumulated by all studied aquatic model food chain organisms increased as the treatment concentrations increased. In addition, these researchers found that, for any given treatment concentration, higher food chain organisms (such as snails and mosquito fish) always contained 1.5 to 2 times more hexachlorobenzene than lower food chain organisms such as algae and daphnids. Furthermore, catfish, being the highest food chain organism in the model aquatic ecosystem, accumulated 10 times more hexachlorobenzene than did any other organisms. Isensee et al. (1976) theorize that either biomagnification within the food chain and/or a species -specific response was important in contributing to the aforementioned accumulation patterns.

Due to the experimental design used by Isensee et al (1976) it is difficult to assess whether biomagnification through food chains was, in fact, occurring, since there is no evidence that the bioaccumulation ratios measured were quantitatively evaluated at equilibrium concentrations.

In a study by Laseter et al. (1976), an experiment was carried out for a duration of one week to determine the difference in uptake of hexachlorobenzene between sunfish (Lepomis macrochirus) held in water free of hexachlorobenzene 16 μg/g and fed sailfin mollies (Poecilia latipinna) contaminated with hexachlorobenzene and sunfish held in water having a concentration of 2.7 μg/l of hexachlorobenzene and fed sailfin mollies contaminated with hexachlorobenzene 16 μg/g. The mean concentration of hexachlorobenzene in the two groups of fish at the end of the experiment was 594 and 3578 μg/l hexachlorobenzene, respectively. From these results, it appeared that aqueous sources contributed far more to the sunfish body burden of hexachlorobenzene than did dietary sources.

Other experiments conducted by Laseter et al. (1976) on uptake and depuration of hexachlorobenzene by various aquatic organisms showed that this chemical was depurated quite rapidly. For example, after 15 days exposure of fingerling bass (6 to 10 cm in length) to concentrations of 2 to 10 μg/l hexachlorobenzene, only 8.6 to 26.9% (depending upon initial exposure concentration) of the residue remained after exposure to water free of hexachlorobenzene for 13 days. Laseter et al. (1976) note that fish initially exposed to lower levels of hexachlorobenzene had succeeded in eliminating a greater proportion of the substance than had those exposed to higher levels.

The findings of Laseter et al. (1976) support the contention that hexachlorobenzene bioaccumulates but does not biomagnify in aquatic food chains. It must be noted, however, that there is no evidence that the relative contributions of aqueous and dietary sources of hexachlorobenzene were measured at equilibrium conditions. It is also uncertain whether predators of fish such as aquatic birds will ultimately biomagnify this compound.

In addition to experimental evidence, there is empirical evidence that hexachlorobenzene has a high potential for accumulation in organisms. Neely et al. (1974) and Metcalf et al. (1973) have shown that the log octanol/water partition coefficient (log P) correlates well with the ability of a compound to accumulate in the lipids of tissues of living organisms. The high log P value of 6.18 (Neely et al. 1974) indicates that the bioaccumulation potential of hexachlorobenzene by aquatic organisms at pollutant concentrations anticipated in environmental waters is very high.

77.4.7 Biotransformation and Biodegradation

In a study on the uptake and excretion of some halogenated aromatic hydrocarbons by juvenile Atlantic salmon (Salmo salar), Zitko et al. (1977) stated that it is generally believed that fish excrete halogenated aromatic hydrocarbons mainly unchanged, at a rate determined primarily by the lipophilicity and/or water solubility of the compounds. In the aquatic model ecosystem of Metcalf et al.(1973) radiolabeled hexachlorobenzene was found in substantial quantities in the various organisms with little evidence of degradation products except "highly polar materials and conjugates". For instance, hexachlorobenzene comprised 85.1 percent of the total radioactivity in alga (Oedogonium cardiacum), 90.8 percent in the snail (Physa sp.), 87.2 percent in the water flea (Daphnia magna), 58.3 percent in mosquito larva (Culex pipiens quinquefasciatus), and 27.2 percent in fish (Gambusia affinis). The aqueous phase of the ecosystem, however, contained an appreciable quantity of pentachlorophenol. This compound was not found in free form in any of the organisms of the system. In the aquatic model ecosystem of Lu and Metcalf (1975) hexachlorobenzene comprised 84 percent of the total radioactivity in the snail, 67 percent in the water flea, 65 percent in mosquito larva, and 64 percent in fish. Pentachlorophenol, however, was found in alga, mosquito larva, and the aqueous phase as the only identified degradation product. Zitko et al. (1977) report that hydroxylated metabolites of halogenated aromatic hydrocarbons appear to play a relatively minor role in the excretion of halogenated aromatic hydrocarbons since the mixed function oxidase system is much less active in fish than in mammals. Zitko et al. (1977) contend that, inasmuch as the mixed function oxidase system has been demonstrated to be induced in trout by PCBs (Lidman et al. 1976), it is likely that most of the polar metabolites of halogenated aromatic hydrocarbons, described in mammals, are also formed in fish but in small amounts which are difficult to detect.

Lu and Metcalf (1975) reported a value for the biodegradability index of hexachlorobenzene of 0.377 in mosquito fish (Gambusia affinis) of the aquatic model ecosystem. The biodegradability index is defined by Lu and Metcalf (1975) as the ratio of polar products of degradation to the non-polar products. A low value for the biodegradability index indicates that a compound resists biodegradation. Comparison of the biodegradability index of hexachlorobenzene with that of some widely studied persistent pollutants, such as DDT and aldrin, give a better idea of the significance of this value. Lu and Metcalf (1975) reported a biodegradability index for DDT of 0.012 in mosquito fish (Gambusia affinis) compared to values of 0.015 for aldrin and 0.377 for hexachlorobenzene.

According to Ware and West (1977), the more highly halogenated a compound becomes, the more resistant it is to biodegradation. Experimental evidence has been found indicating that chlorobenzene is a persistent compound (Lu and Metcalf 1975) and is not readily biodegraded unless the microorganisms present are already growing on another hydrocarbon source (Gibson et al. 1968). Furthermore, Alexander and Lustigman (1966) found that the presence of a chlorine atom on the benzene ring retarded the rate of biodegradation. On these bases, hexachlorobenzene, being more highly chlorinated than chlorobenzene, would presumably biodegrade more slowly than chlorobenzene under similar conditions of exposure to microorganisms.

77.5 Data Summary

Data found concerning the processes for removal of hexachlorobenzene are insufficient to allow designation of a most probable fate pathway for this compound. Hexachlorobenzene has a high affinity for lipophilic materials; consequently, sorption and bioaccumulation are anticipated to occur quite readily. It appears that the major portion of hexachlorobenzene found in aquatic organisms is from aqueous rather than dietary sources. Furthermore, experimentally determined rates of depuration of hexachlorobenzene appear to be substantially more rapid than rates of depuration for other persistent chemicals, such as DDT. Consequently, biomagnification of hexachlorobenzene through aquatic food chains probably does not occur. Not enough data however is available to determine if this statement is true where birds are the predators of fish. These data are summarized in Table 77-2.

Table 77-2

Summary of Aquatic Fate of Hexachlorobenzene

Environmental Process[a]	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Does not occur readily.	-	-	Medium
Oxidation	Does not occur at ambient conditions.	-	-	High
Hydrolysis	Does not occur in ambient waters.	-	-	High
Volatilization	Probably volatilizes relatively slowly due to the low vapor pressure; no specific information found.	-	-	Low
Sorption	Sorption processes appear to be very important.	-	-	Medium
Bioaccumulation	The majority of hexachlorobenzene found in aquatic organisms is from aqueous rather than dietary sources; probably does not biomagnify.	-	-	High
Biotransformation/ Biodegradation	Biodegrades extremely slowly, if at all.	-	-	High

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[a] There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

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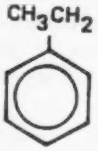
78. ETHYLBENZENE

78.1 Statement of Probable Fate

From the available data it would appear that the principal mechanism for removal of ethylbenzene from the aquatic environment is volatilization. The atmospheric photodestruction of ethylbenzene probably overshadows all other fates. Adsorption on sediments and suspended solids appears to play a role that cannot be established quantitatively at this time. It is not possible to estimate the relative importance of biodegradation in the determination of the fate of ethylbenzene in the aquatic environment.

78.2 Identification

Ethylbenzene has been detected at several geographical locations in finished drinking water, effluents, and ambient surface waters (Shackelford and Keith 1976). The chemical structure of ethylbenzene is shown below.



Ethylbenzene

CAS NO. 100-41-4
TSL NO. DA 07000

Alternate Names

Phenylethane
Ethylbenzol

78.3 Physical Properties

The general physical properties of ethylbenzene are as follows.

Molecular weight (Verschueren 1977)	106.16
Melting point (Verschueren 1977)	-94.9°C
Boiling point (Verschueren 1977)	136.2°C
Vapor pressure at 20°C (Verschueren 1977)	7 torr

Solubility in water at 20°C (Verschueren 1977)	152 mg/l
Log octanol/water partition coefficient (Tute 1971)	3.15

78.4 Summary of Fate Data

78.4.1 Photolysis

Inasmuch as the main transport process for ethylbenzene appears to be volatilization, which removes it from water, the atmospheric destruction of ethylbenzene probably subordinates all other fate processes. These complex photochemical reactions have been studied in simulated smog chambers (Altshuller et al. 1962; Laity et al. 1973) that measured the rate of disappearance of the volatilized organic material. The half-conversion time of m-xylene and 1,3,5-trimethylbenzene have been reported to be somewhat less than four hours (Altshuller et al. 1962). From this value and the table of relative reactivities given by Laity et al. (1973), it can be inferred that the corresponding half-conversion time for ethylbenzene would be approximately 15 hours. The temporal stability of ethylbenzene under actual atmospheric conditions is, as yet, unknown. Experiments performed in laboratory irradiation chambers are usually conducted for relatively short periods and cannot account for all of the meteorological variables within a natural airshed.

78.4.2 Oxidation

Ethylbenzene is readily oxidized in the liquid phase by molecular oxygen, but this oxidation is effectively inhibited by the presence of water (Stephens and Roduta 1935). No data were found from which a relevant rate of oxidation of ethylbenzene in environmental waters could be determined with confidence.

78.4.3 Hydrolysis

No data have been found that would support any role for hydrolysis at ambient environmental conditions.

78.4.4 Volatilization

From the vapor pressure data (Gray 1957) and the aqueous solubility (Verschueren 1977), the computed Henry constant ($H = 6.44$ atmos. m^3 $mole^{-1}$) lies in the same range as that for toluene, ($H_{tol} = 6.68$ atmos. m^3 $mole^{-1}$) (Mackay and Leinonen 1975). Therefore, the half-life with respect to volatilization (from a water layer one meter thick) could approximate the 5 to 6 hour half-life estimated by Mackay and Leinonen (1975) for toluene. Thus, volatilization is probably an important removal process for ethylbenzene from the aquatic environment. No experimental data on rates of evaporation of ethylbenzene from water were found.

78.4.5 Sorption

Although no specific environmental sorption studies were found in the reviewed literature, the log octanol/water partition coefficient (log P=3.15, Tute 1971) indicates that sorption processes may be significant for ethylbenzene. Presumably, ethylbenzene will be adsorbed by sedimentary organic material; however, the extent to which this adsorption will interfere with volatilization has not been considered.

78.4.6 Bioaccumulation

No information was found indicating that ethylbenzene would bioaccumulate. Moreover, Metcalf and Sanborn (1975) maintain that compounds with solubilities of 50 mg/l or more generally have little potential for aquatic bioaccumulation.

78.4.7 Biotransformation and Biodegradation

Some species of soil bacteria have been demonstrated to be capable of using ethylbenzene as a sole carbon source (Claus and Walker 1964; Gibson *et al*. 1966). This microbial oxidative degradation proceeds via hydroxylation of the aromatic ring to 2,3-dihydroxy-1-ethylbenzene (Gibson *et al*. 1973).

78.5 Data Summary

The data obtained for ethylbenzene are summarized in Table 78-1. Volatilization appears to be the major route of removal of this chemical from aquatic environments. The atmospheric reactions of ethylbenzene probably overshadow all other fate processes. The estimated photooxidative half-life in Table 78-1 is based on smog chamber data and is, therefore, an approximation applicable only to a metropolitan environment.

Table 78-1

Summary of Aquatic Fate of Ethylbenzene

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Direct photolytic cleavage is energetically improbable in the troposphere.	-	-	Low
Oxidation[a]	Probably not important as an aquatic fate; however, atmospheric photooxidation is probably the main fate process.	-	~15 hr.	Low
Hydrolysis	Not aquatically significant.	-	-	High
Volatilization	Significant transport process responsible for removal of ethylbenzene from water.	-	5 - 6 hr.	Low
Sorption	Relative importance cannot be determined.	-	-	Low
Bioaccumulation	Probably not important.	-	-	Low
Biotransformation/ Biodegradation	Relative importance cannot be determined.	-	-	Low

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[a] The predominant environmental process which is thought to determine the fate of the compound.

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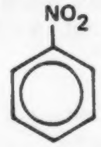
79. NITROBENZENE

79.1 Statement of Probable Fate

The aquatic fate of nitrobenzene might involve both photoreduction of the nitro group and biodegradation. It is not possible with the available data, to determine which of these two fates predominates. It should be noted that both photochemical and biological degradation can lead potentially to a large variety of organic nitrogen compounds, two of which, namely, diphenylhydrazine and benzidine, are presently listed as priority pollutants. The persistence of these compounds, as well as nitrobenzene itself, cannot be ascertained from existing data.

79.2 Identification

Nitrobenzene has been found in unfinished drinking water and ambient water (Shackelford and Keith 1976). The chemical structure of nitrobenzene is shown below.



Nitrobenzene

CAS NO. 98-95-3
TSL NO. DA 64750

Alternate Names

Nitrobenzol

79.3 Physical Properties

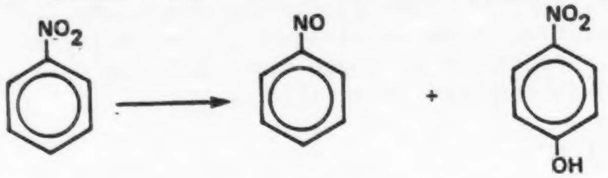
The general physical properties of nitrobenzene are as follows.

Molecular weight (Windholz 1976)	123.11
Melting point (Windholz 1976)	5.6°C
Boiling point at 760 torr (Windholz 1976)	211°C
Vapor pressure at 20°C (Vershueren 1977)	0.15 torr
Solubility in water at 20°C (Verschueren 1977)	1900 mg/1
Log octanol/water partition coefficient (Neely *et al*. 1974)	1.85

79.4 Summary of Fate Data

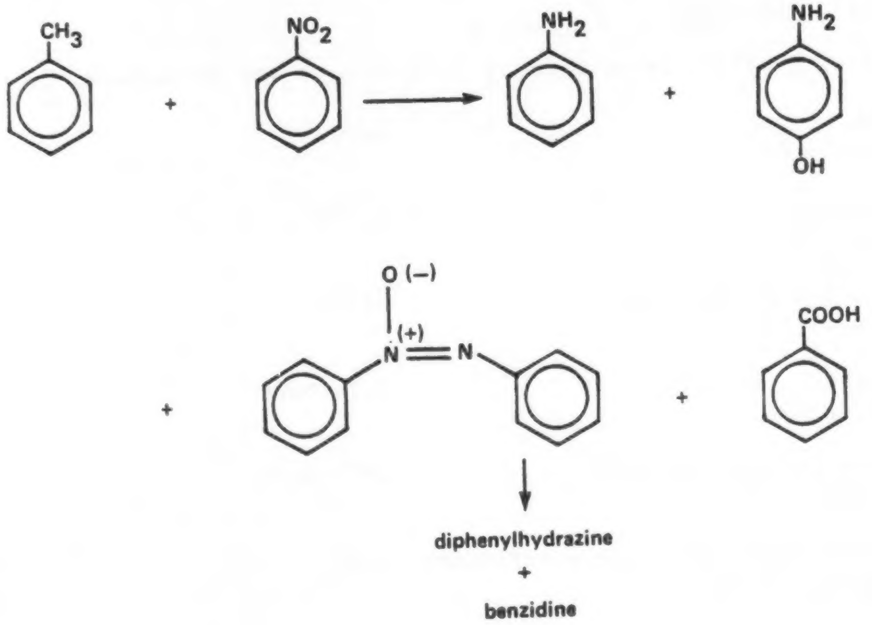
79.4.1 Photolysis

Although dissociation of an N-O nitro bond by light of wavelengths longer than 190 nm is energetically improbable, photoreduction of aromatic nitrocompounds occurs at least to 436 nm (Leighton and Lucy 1934; Morrison 1969). The vapor phase irradiation products of nitrobenzene are nitrosobenzene and 4-nitrophenol (Hastings and Matsen 1948).



Inasmuch as the quantum yield of this vapor-phase reaction can be expected to be quite low (Morrison 1969) and evaporation of nitrobenzene from water is not thought to be a major aquatic transport process (see Section 79.4.4, Volatilization), there is little likelihood that vapor-phase photolysis or photooxidation will make a significant contribution to the aquatic fate of this compound.

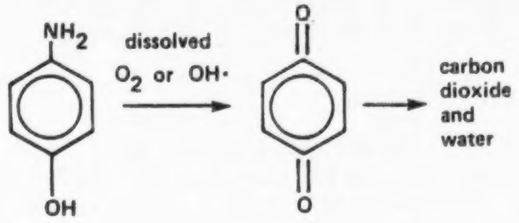
In the liquid phase, nitrobenzene has been demonstrated to photooxidize suitable hydrogen donors (Morrison 1969). For example, exposure of nitrobenzene and toluene to sunlight leads to the formation of a complex mixture, the principal compounds of which are aniline, 4-aminophenol, azoxybenzene and benzoic acid (Vecchiotti and Zanetti 1931; Morrison 1969).



Adsorption of nitrobenzene by humus could allow reactions of this type to play a significant role in the abiotic, aquatic fate of this compound. The most suitable hydrogen donors appear to be alkylaromatics that can form benzyl-type radicals, although aromatic hydrogens are also reported to be abstracted (Morrison 1969). In this respect, suspended humus should have an abundance of reaction sites (Rook 1977) for the photoreduction of nitrobenzene.

79.4.2 Oxidation

Although no specific environmental data regarding oxidation were found, it is probable that oxidation does not operate as an initial aquatic fate process for nitrobenzene. Substitution by nitro groups decreases the electron density of aromatic rings (Fieser and Fieser 1956) resulting in a decreased susceptibility to attack by molecular oxygen and hydroxyl radicals. Nitrobenzene itself is a strong chemical oxidizing agent, but intramolecular oxidation-reduction reactions involving the aromatic hydrogens are unknown; an intermolecular oxidation-reduction reaction, however, has been postulated as the mechanism of its vapor-phase photolysis (Morrison 1969). Oxidative processes undoubtedly contribute, via quinone formation (Cason 1948), to the ultimate destruction of nitrobenzene's photoreduction products.



79.4.3 Hydrolysis

No specific information was found regarding the hydrolysis of nitrobenzene. Nonetheless, the hydrolytic scission of any covalent bond of nitrobenzene under ambient environmental conditions is highly improbable (Fieser and Fieser 1956).

79.4.4 Volatilization

The vapor pressure data for nitrobenzene (Gray 1957) may be extended to ambient temperature using the equation:

$\ln VP = a + b/T$ (where VP is in torr; T in °K)

from which the value included in Section 79.3 was derived using $a = 20.2$ and $b = 6415$. Further, the solubility of nitrobenzene in water is given as 1900 mg/l (Verscnueren 1977). Combining these data, the calculated Henry constant for nitrobenzene, $H = 1.53 \times 10^{-5}$ atmos. m^3 $mole^{-1}$, is comparable to that of aldrin (Mackay and Leinonen 1975) for which the half-life with respect to volatilization from water is approximately 185 hours. Under these circumstances, it would appear that volatilization, while contributing to the transport of nitrobenzene, will probably not be of overbearing consequence. In the model aquatic ecosystem, studied by Lu and Metcalf (1975), 2.22 percent of the nitrobenzene introduced into the water was recovered in the air at the end of the experiment.

79.4.5 Sorption

The octanol/water partition coefficient for nitrobenzene, corresponding to log p = 1.85 (Neely et al. 1974), suggests only a limited preference for lipophilic organic materials over water. No data on adsorptive transport or removal of nitrobenzene from water were found. The polar nature of the nitro group, however, coupled with nitrobenzene's miscibility with most organic material, insures the adsorption of nitrobenzene by humus. Adsorption onto clay is also thought to be very highly probable. Photoreduction on humus, and acid-base catalyzed reactions of the reduction products on clay, could be a major fate pathway for nitrobenzene.

79.4.6 Bioaccumulation

Radio-labelled nitrobenzene was studied for its effect in a model aquatic ecosystem developed by Lu and Metcalf (1975). This aquatic ecosystem was devised for studying relatively volatile organic compounds and simulating direct discharge of chemical wastes. The food chain members consisted of green filamentous algae, snails, water fleas, mosquito larvae, and fish.

The contaminative efficacy of nitrobenzene was evaluated by determining the quantitative distribution of the radioactivity in the organisms, water, and air of the model aquatic ecosystem. Nitrobenzene was neither stored nor ecologically magnified, (ecological magnification of 29) and it was found to be resistant to degradation (biodegradability index of 0.023). Compared to halogenated organic compounds, such as hexachlorobenzenes and DDT, nitrobenzene was found less likely to be stored in the fatty tissue of aquatic organisms.

79.4.7 Biotransformation and Biodegradation

A nitro substituent generally decreases the biodegradability of aromatic rings (Venulet and Van Etten 1970; Lu and Metcalf 1975), and it has been reported that the decomposition of nitrobenzene by soil microflora requires at least 64 days (Verschueren 1977).

The metabolism of C14 labeled nitrobenzene by rabbits has been extensively investigated (Robinson *et al*. 1951; Parke 1956). Fifty-eight percent of the label was eliminated in the urine, with 31 percent being present as aminophenol and its detoxification conjugates. The conjugates were largely the glucuronide or the N-acetyl derivative of the glucuronide. In addition, detoxification conjugates of 3-nitrophenol, 4-nitrophenol, and aniline were also isolated from the urine.

79.5 Data Summary

Table 79-1 summarizes the aquatic fate data discussed above for nitrobenzene. Photoreduction of the nitro group and/or hydroxylation of the ring while adsorbed on humus could be an important abiotic fate. Biodegradation to the same type of reduction products could also be an important fate process. There is no way, with the available data, to ascertain which of these two fates predominates. It should be noted that both photochemical and biological degradation can lead potentially to a large variety of organic nitrogen compounds, two of which, namely, diphenylhydrazine and benzidine, are presently listed as priority pollutants.

Table 79-1

Summary of Aquatic Fate of Nitrobenzene

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis[a]	May be a significant process if it is adsorbed on humus near the air-water surface.	-	-	Medium
Oxidation	Highly improbable	-	-	High
Hydrolysis	Highly improbable	-	-	High
Volatilization	Unlikely to be a significant contributing transport process.	-	~200 hours(e)[b]	Medium
Sorption	Adsorption may provide a possibly important reaction site; no specific experimental data.	-	-	Medium
Bioaccumulation	Does not appear to be important.	-	-	High
Biotransformation/ Biodegradation[a]	Slow but could be significant in the absence of appreciable photolysis.	-	-	Medium

---

a. The most probable fate processes are photolysis and biodegradation. Available data are insufficient for a more definitive statement.

b. Based on a comparison to the value calculated for aldrin by Mackay and Leinonen (1975).

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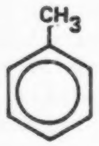
80. TOLUENE

80.1 Statement of Probable Fate

From the available data it appears that the principal mechanism for removal of toluene from the aquatic environment is volatilization. The atmospheric photodestruction of toluene probably subordinates all other fates. Adsorption on sediments and suspended solids probably plays a role in the fate of toluene, but it cannot be established quantitatively at this time. The data do not allow the estimation of the relative importance of biodegradation in the determination of the fate of toluene in the aquatic environment.

80.2 Identification

Toluene has been detected at several geographical locations in finished drinking water, industrial effluents, and ambient surface waters (Shackelford and Keith 1976). The structure of toluene is shown below.



Toluene

CAS NO. 108-88-3
TSL NO. XS 52500

Alternate Names

Toluol
Phenylmethane
Methylbenzene
Methylbenzol
Methacide

80.3 Physical Properties

The general physical properties of toluene are as follows.

Molecular weight (Weast 1977)	92.13
Melting point (Weast 1977)	-95°C
Boiling point (Weast 1977)	110.6°C

Vapor pressure at 25°C (Weast 1977)	28.7 torr
Solubility in water at 25°C (Sutton and Calder 1975)	534.8 mg/l
Log octanol/water partition coefficient (Tute 1971)	2.69

80.4 Summary of Fate Data

80.4.1 Photolysis

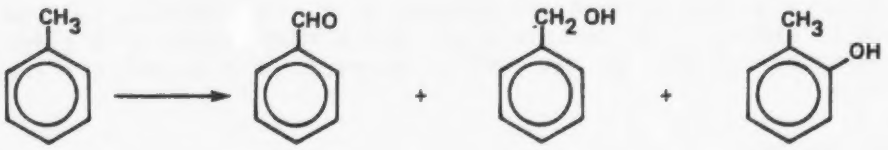
The predominant photochemical reaction of toluene is generally regarded as a dissociation with formation of benzyl radical (Porter and Norman 1954). Reaction of this benzyl radical with molecular oxygen is reported to be extremely fast ($k \sim 10^9$ l mole sec^{-1}) resulting in the production of benzyl hydroperoxide. Although benzyl hydroperoxide is thermally stable, it can be photochemically dissociated to benzyl alcohol and benzaldehyde.

Toluene itself does not absorb light at wavelengths longer than 286 nm, but a charge-transfer complex between toluene and molecular oxygen absorbs electromagnetic radiation to at least 350 nm. According to Wei and Adelman (1969), it is the photolysis of this charge-transfer complex that is responsible for the observed oxidation products (benzyl alcohol and benzaldehyde) at ambient conditions. No information was found on the extent of formation of this complex in water. Furthermore, no information was found from which the rate of benzylic hydrogen abstraction in water could be determined.

Inasmuch as the main transport process removing toluene from water appears to be volatilization, the atmospheric reactions of toluene probably subordinate all other fate processes. These complex photochemical reactions have been studied in simulated smog chambers (Altshuller *et al.* 1962; Laity *et al.* 1973) that measured the rate of disappearance of the volatilized organic material. The half-conversion time of m-xylene and 1,3,5-trimethylbenzene have been reported to be somewhat less than four hours (Altshuller *et al.* 1962). From this value and the table of relative reactivities given by Laity *et al.* (1973), it can be inferred that the corresponding half-conversion time for toluene would be approximately fifteen hours. Benzaldehyde is reported to be the principal organic product from the photochemical reaction of toluene (Laity *et al.* 1973). The temporal stability of toluene under actual atmospheric conditions is, as yet, unknown. Experiments performed in laboratory irradiation chambers are usually conducted for relatively short periods and cannot account for all of the meteorological variables within a natural airshed.

80.4.2 Oxidation

Toluene is readily oxidized in the liquid phase by molecular oxygen, but this oxidation is effectively inhibited by the presence of water (Stephens and Roduta 1935). Reaction of toluene in water with hydroxyl radicals from the irradiation of hydrogen peroxide produces benzaldehyde, benzyl alcohol, and an isomeric mixture of cresols (Jefcoate et al. 1969). No data were found from which a relevant rate of oxidation of toluene in environmental waters could be determined.



80.4.3 Hydrolysis

No data have been found that would support any role for hydrolysis at ambient environmental conditions.

80.4.4 Volatilization

The half-life with respect to volatilization from a water column one meter thick has been estimated by Mackay and Leinonen (1975) to be 5.18 hr for toluene. Some assumptions made in this estimation were: 1) the contaminant concentration is in solution, rather than in suspended, colloidal, ionic, complexed, or adsorbed form; 2) the vapor is in equilibrium with the liquid at the interface; 3) water diffusion or mixing is sufficiently rapid so that the concentration at the interface approaches that of the bulk of the water; and 4) the rate of evaporation of water is negligibly affected by the presence of the contaminants.

80.4.5 Sorption

Although no specific environmental sorption studies were found in the reviewed literature, the log octanol/water partition coefficient (log $P= 2.69$; Tute 1971) indicates that sorption processes may be significant for toluene. Presumably, toluene will be adsorbed by sedimentary organic material, but the extent to which this absorption will interfere with volatilization has not been considered.

80.4.6 Bioaccumulation

No information was found indicating that toluene would bioaccumulate. Moreover, Metcalf and Sanborn (1975) maintain that, in general, compounds with solubilities of 50 mg/l or more have little potential for aquatic bioaccumulation.

80.4.7 Biotransformation and Biodegradation

Some species of soil bacteria have been demonstrated to be capable of using toluene as a sole carbon source (Claus and Walker 1964; Gibson *et al*. 1966). This oxidative microbial degradation proceeds via hydroxylation of the aromatic ring to a mixture of cresols and catechols, which are metabolized further to acetic acid and pyruvic acid. In mammals, toluene is detoxified by oxidation to benzoic acid, which then reacts with glycine to form hippuric acid (Ogata *et al*. 1970). Hippuric acid is rapidly excreted in the urine.

80.5 Data Summary

The data obtained for toluene are summarized in Table 80-1. Volatilization appears to be the major route of removal of this chemical from aquatic environments. The atmospheric reactions of toluene probably subordinate all other fate processes. The precipitation of the atmospheric oxidation products could introduce benzaldehyde into the water. The estimated photooxidative half-life in Table 80-1 is based on smog chamber data and is, therefore, an approximation applicable only to a metropolitan environment.

Table 80-1

Summary of Aquatic Fate of Toluene

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Direct photolytic cleavage is energetically improbable in the troposphere.	-	-	Medium
Oxidation[a]	Probably not important as an aquatic fate; however, atmospheric photooxidation subordinates all other fate processes.	-	~15 hrs.	Medium
Hydrolysis	Not aquatically significant	-	-	High
Volatilization	Significant transport process responsible for removal of toluene from water.	0.193 hr^{-1}	5.18 hrs.	Medium
Sorption	Relative importance cannot be determined.	-	-	Low
Bioaccumulation	Probably not important.	-	-	Low
Biotransformation/ Biodegradation	Relative importance cannot be determined.	-	-	Low

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[a] The predominant environmental process which is thought to determine the fate of the compound.

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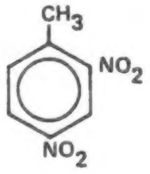
81. 2,4-DINITROTOLUENE

81.1 Statement of Probable Fate

The aquatic fate of 2,4-dinitrotoluene might involve photodestruction, oxidation, and biodegradation. It is not possible, with the available data, to determine which of these fates predominates. Adsorption onto sediment probably plays a major role in transport and may also provide reaction sites for destruction. It should be noted that both abiotic and biotic degradation can lead potentially to a large variety of organic nitrogen compounds. The persistence of these compounds, as well as 2,4-dinitrotoluene itself, cannot be ascertained from existing data.

81.2 Identification

2,4-Dinitrotoluene has been detected in ambient waters and industrial effluents (Shackelford and Keith 1976). The chemical structure of 2,4-dinitrotoluene is shown below.



2,4-Dinitrotoluene

CAS NO. 121-14-2
TSL NO. XT 15750

Alternate Names

Dinitrotoluol
DNT
1-Methyl-2,4-dinitrobenzene

81.3 Physical Properties

The general physical properties of 2,4-dinitrotoluene are as follows.

Molecular weight (Verschueren 1977)	182.14
Melting point (Verschueren 1977)	70°C
Boiling point at 760 torr (Verschueren 1977)	300°C
Vapor pressure at 59°C (Lenchitz and Velicky 1970)	0.0013 torr

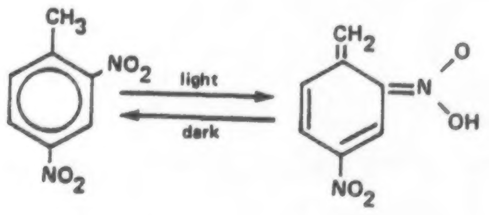
Solubility in water at 22°C (Verschueren 1977)	270 mg/1
Log octanol/water partition coefficient (Calc. by method of Tute 1971)	2.01

81.4 Summary of Fate Data

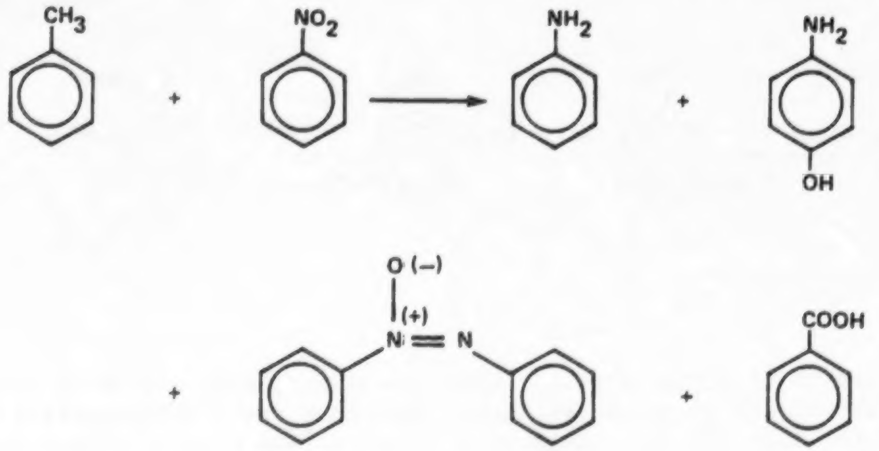
81.4.1 Photolysis

Although dissociation of an N-O nitro bond by light of wavelengths longer than 190 nm is energetically improbable, photoreduction of aromatic nitro compounds occurs at least to 436 nm (Leighton and Lucy 1934; Morrison 1969). It is not expected that vapor phase photolysis of 2,4-dinitrotoluene will have any significant effect on its aquatic fate in view of the compound's low volatility and moderate solubility. Photolysis in solution, however, may be a highly probable fate process.

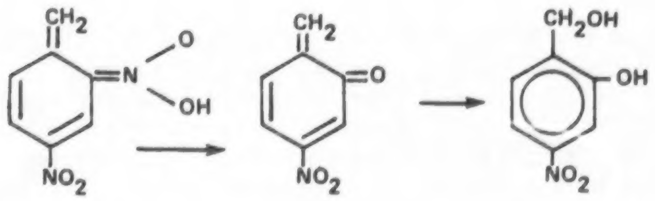
Wettermark (1962) demonstrated that 2,4-dinitrotoluene is photochromic, i.e., it has the property of becoming colored on exposure to light and then becoming colorless in the dark. When dilute aqueous solutions (10^{-4}M) of 2-nitrotoluene, or any of several, similar compounds including 2,4-dinitrotoluene, are irradiated with ultraviolet light they become intensely colored and then slowly fade with the cessation of irradiation. Although the absorption of light of wavelengths longer than 330 nm is greatly diminished in the case of 2-nitrotoluene and 2,4-dinitrotoluene, absorption still does occur. The photochromism of these compounds appears to be dependent on the ease of formation of a structural isomer analogous to an *aci*-nitroparaffin.



The environmental consequence of this phenomenon should be the reduction, in sunlight, of the nitro group to a hydroxylamino, nitroso, or amino group with concomitant oxidation of the methyl group to an alcohol, aldehyde, or carboxylic acid group. Specific substantiation for this supposition has not been found, thus far, in the reviewed literature. The exposure to sunlight, however, of a mixture of nitrobenzene and toluene has been shown to lead to a complex mixture, the principal compounds of which are aniline, 4-aminophenol, azoxybenzene, and benzoic acid (Vecchiotti and Zanetti 1931; Morrison 1969).



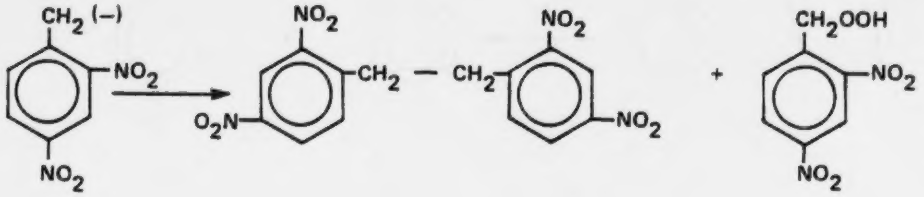
Adsorption of 2,4-dinitrotoluene on a suspended clay particle, or its incorporation into an acidic micelle, could provide an additional degradative pathway for the initial photoproduct. Since aci-nitroparaffins undergo acid catalyzed hydrolysis to olefinic carbonyl compounds (Johnson and Degering 1943), the following sequence might take place.



81.4.2 Oxidation

Oxidation of the methyl group of 2,4-dinitrotoluene by aqueous hydroxyl radical or dissolved oxygen is a distinct environmental possibility. In very strongly basic hydroxylic solvents, the benzyl anion of 2,4-dinitrotoluene transfers an electron to molecular oxygen or any other available electron acceptor to form the 2,4-dinitrobenzyl radical

(Russell et al. 1967). This organic radical can then couple to form 2,2',4,4'-tetranitrobibenzyl or react further with oxygen to form a hydroperoxide. Further sequential oxidation of these two compounds leads to a mixture of oxidation products.



Since it is highly probable that 2,4-dinitrotoluene will be adsorbed by suspended clay particles, these reactions are environmentally feasible on the clay surface, inasmuch as this surface provides basic reaction sites for ionization.

81.4.3 Hydrolysis

There is little likelihood that direct hydrolysis of this compound will occur. No data were found suggesting that dinitrotoluenes are subject to hydrolysis under environmental conditions.

81.4.4 Volatilization

Since the vapor pressure of 2,4-dinitrotoluene is quite low at ambient conditions and the solubility is moderate (270 mg/l at 22°C) (Verschueren 1977), it is anticipated that the Henry constant will be within the range of 1×10^{-5} to 1×10^{-6} atmos. m^3 $mole^{-1}$. These values indicate that the half-life with respect to volatilization will be approximately hundreds of days (Mackay and Leinonen 1975). Volatilization, therefore, is probably not an important transport process for 2,4-dinitrotoluene.

81.4.5 Sorption

The log octanol/water partition coefficient calculated by the method of Tute (1971) (log P =2.01) is sufficiently large to indicate that adsorption by humus may be significant for 2,4-dinitrotoluene. Although no data were found specifically pertaining to adsorption of this compound, the ability of polynitroaromatic compounds to form very stable charge-transfer complexes with more highly electronegative aromatic compounds (Hall and Poranski 1970) indicates that 2,4-dinitrotoluene should be strongly adsorbed by both humus and clay. In addition, the basic sites on the clay surface might form addition-type complexes with this compound (Hall and Poranski 1970).

81.4.6 Bioaccumulation

No environmentally relevant data on the bioaccumulation of 2,4-dinitrotoluene have been found. By analogy with nitrobenzene, bioaccumulation may not be an important process, and this contention is supported by the relatively low octanol/water partition coefficient (log P = 2.01) for 2,4-dinitrotoluene compared to highly bioaccumulated compounds (PCBs, for example) which exhibit log P value of 5 to 6 or more.

81.4.7 Biotransformation and Biodegradation

Detoxification of 2-nitrotoluene by dogs leads to urinary excretion of 2-nitrobenzyl alcohol and 2-nitrobenzoic acid (Venulet and VanEtten 1970); 2,4-Dinitrotoluene might be metabolized in an analogous fashion. Alexander and Lustigman (1966) report that dinitrobenzenes are resistant to biodegradation by soil microorganisms. It has been reported that dinitrotoluenes are decomposed very slowly in a reservoir (Galuzova 1963). Biodegradation by *Azotobacter* has also been reported to be slow (Bringmann and Kuehn 1972). Reduction of the nitro groups by the fungus *Mucrosporium* has been reported to result in the formation of 2-amino-4-nitrotoluene, 4-amino-2-nitrotoluene, 2,2'-dinitro-4,4'-azoxytoluene, 4,4'-dinitro-2,2'-azoxytoluene, and 4-acetamido-2-nitrotoluene (McCormick *et al.* 1978).

81.5 Data Summary

Table 81-1 summarizes the aquatic fate data discussed above for 2,4-dinitrotoluene. Intramolecular photolysis, oxidation by dissolved oxygen, and, to a small extent, biodegradation may all be aquatic fates for this compound. Adsorption onto sediment probably plays a major role in transport and may also provide reaction sites for destruction. With the available data, it is not possible to determine which fate predominates.

Table 81-1

Summary of Aquatic Fate of 2,4-Dinitrotoluene

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis[a]	Probably responsible for color development in muntition plant effluents.	-	-	High
Oxidation[a]	May be important in highly aerated waters.	-	-	Low
Hydrolysis	Highly improbable based on the compound's resistance to electrophilic attack.	-	-	Medium
Volatilization	No specific data found; probably not important.	-	-	Medium
Sorption	Interaction with sediments highly probable with the possibility of stable complex formation.	-	-	Medium
Bioaccumulation	Importance not known.	-	-	Low
Biotransformation/[a] Biodegradation	Slow but could be significant depending upon relative rates of other fate processes.	-	-	Low

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[a] Since intramolecular photolysis, oxidation by dissolved oxygen, and biodegradation may all be aquatic fates for this compound, no predominant fate was assigned.

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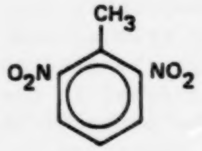
82. 2,6-DINITROTOLUENE

82.1 Statement of Probable Fate

The aquatic fate of 2,6-dinitrotoluene may involve both photodestruction and biodegradation. It is not possible, with the available data, to determine which of these fates predominates. Adsorption onto sediment probably plays a major role in transport and may also provide reaction sites for destruction. It should be noted that both abiotic and biotic degradation can lead potentially to a large number of organic nitrogen compounds. The persistence of these compounds, as well as 2,6-dinitrotoluene itself, cannot be ascertained from existing data.

82.2 Identification

2,6-Dinitrotoluene, a relatively minor intermediate in the manufacture of trinitrotoluene (Fieser and Fieser 1956), has been detected in finished drinking water, industrial effluents, and ambient waters (Shackelford and Keith 1976). The chemical structure of 2,6-dinitrotoluene is shown below.



2,6-Dinitrotoluene

CAS NO. 606-20-2
TSL NO. XT 19250

Alternate Names

Dinitrotoluol

82.3 Physical Properties

The general physical properties of 2,6-dinitrotoluene are as follows.

Molecular weight (Weast 1977)	182.14
Melting point (Weast 1977)	65°C
Boiling point (Maksimov 1968)	285°C
Vapor pressure	No data found

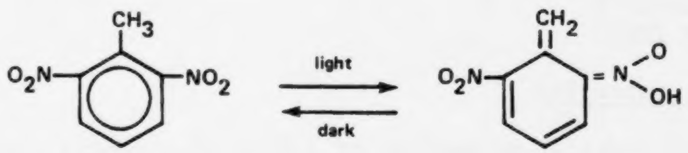
Solubility in water	No data found
Log octanol/water partition coefficient (Calc. by method of Tute 1971)	2.05

82.4 Summary of Fate Data

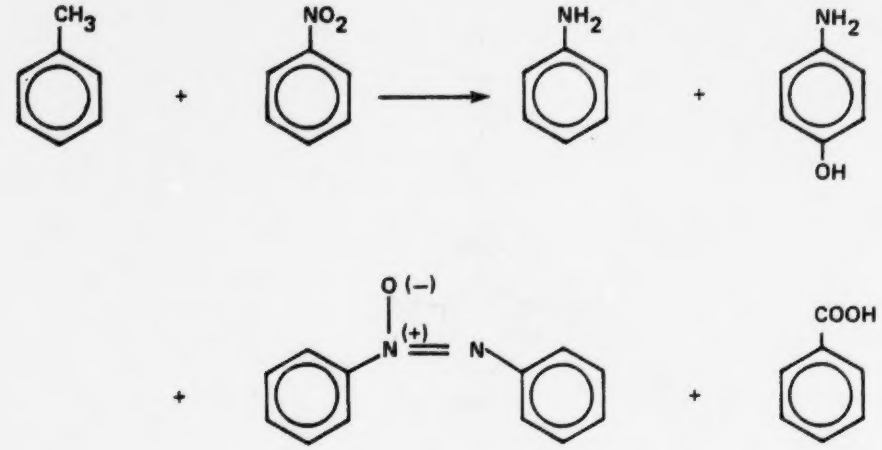
82.4.1 Photolysis

Although dissociation of an N-O nitro bond by light of wavelengths longer than 190 nm is energetically improbable, photoreduction of aromatic nitro compounds occurs at least to 436 nm (Leighton and Lucy 1934; Morrison 1969). It is not expected that vapor-phase photolysis of 2,6-dinitrotoluene will have any significant effect on its aquatic fate in view of the compound's expected low volatility and moderate solubility. Photolysis in solution, however, may be a highly probable fate process.

Wettermark (1962) demonstrated that 2,6-dinitrotoluene is photochromic, i.e., it has the property of becoming colored on exposure to light and then becoming colorless in the dark. When dilute aqueous solutions (10^{-4}M) of 2-nitrotoluene, or any of several similar compounds, are irradiated with ultraviolet light they become intensely colored and then slowly fade with the cessation of irradiation. Although the absorption of light of wavelengths longer than 330 nm is greatly diminished in the case of 2,6-dinitrotoluene, absorption still does occur. The photochromism of these compounds appears to be dependent on the ease of formation of a structural isomer analogous to an *aci*-nitroparaffin.

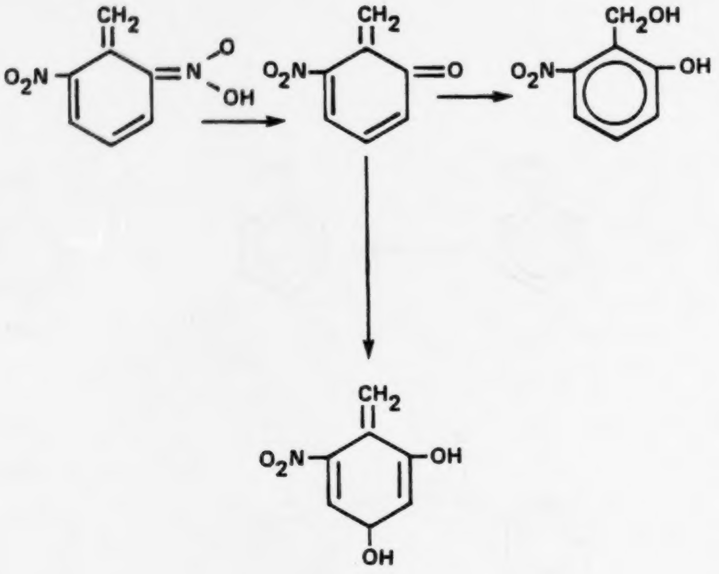


The environmental consequence of this phenomenon should be the reduction, in sunlight, of the nitro group to a hydroxylamino, nitroso, or amino group with concomitant oxidation of the methyl group to an alcohol, aldehyde, or carboxylic acid group. Specific substantiation for this supposition has not been found, thus far, in the reviewed literature. The exposure to sunlight, however, of a mixture of nitrobenzene and toluene has been shown to lead to a complex mixture, the principal compounds of which are aniline, 4-aminophenol, azoxybenzene, and benzoic acid (Vecchiotti and Zanetti 1931; Morrison 1969).



CH3
NO2
NH2
NH2
OH
O (−)
N
(+)
N
COOH

Adsorption of 2,6-dinitrotoluene on a suspended clay particle, or its incorporation into an acidic micelle, could provide an additional degradative pathway for the initial photoproduct. Since aci-nitroparaffins undergo acid catalyzed hydrolysis to olefinic carbonyl compounds (Johnson and Degering 1943), the following sequence might take place.



82.4.2 Oxidation

Oxidation of the methyl group of 2,6-dinitrotoluene by aqueous hydroxyl radical or dissolved oxygen is not environmentally feasible. In very strongly basic solutions, the benzyl anion of 2,6-dinitrotoluene has been observed to be very stable to oxidation by dissolved oxygen (Russell et al. 1967).

82.4.3 Hydrolysis

No data were found suggesting that the dinitrotoluenes are subject to hydrolysis under environmental conditions.

82.4.4 Volatilization

The vapor pressure of the dinitrotoluenes is probably low at ambient conditions and the solubility is expected to be moderate, perhaps about 300 ppm (by inference from the reported solubility of the 2,4-isomer in Verschueren 1977). From this it is anticipated that the Henry constant for the 2,6-isomer will be in the range of 1×10^{-5} to 1×10^{-6} atmos. m^3 $mole^{-1}$. This would suggest that the half-life with respect to volatilization would be measured in hundreds of days (Mackay and Leinonen 1975). Volatilization, therefore, may not be an important transport process for 2,6-dinitrotoluene. No experimental data, however, were found to support this supposition.

82.4.5 Sorption

The log/octanol water partition coefficient calculated by the method of Tute (1971) (log P = 2.05) is sufficiently large to indicate that adsorption by humus may be significant for 2,6-dinitrotoluene. Although no data were found specifically pertaining to adsorption of this compound, the ability of polynitroaromatic compounds to form very stable charge-transfer complexes with more highly electronegative aromatic compounds (Hall and Poranski 1970) indicates that 2,6-dinitrotoluene should be strongly adsorbed by both humus and clay. In addition, the basic sites on the clay surface might form addition-type complexes with this compound (Hall and Poranski 1970).

82.4.6 Bioaccumulation

No environmentally relevant data on the bioaccumulation of 2,6-dinitrotoluene have been found. By analogy with nitrobenzene, bioaccumulation may not be an important process; this contention is supported by the relatively low value of the log octanol/water partition coefficient for 2,6-dinitrotoluene (log P = 2.05) compared to log P values of 5 to 6 or more for strongly bioaccumulated compounds (PCBs, for example).

82.4.7 Biotransformation and Biodegradation

Detoxification of 2-nitrotoluene by dogs leads to urinary excretion of 2-nitrobenzyl alcohol and 2-nitrobenzoic acid (Venulet and VanEtten 1970). Similarly, 2,6-dinitrotoluene might be metabolized in an analogous fashion. Alexander and Lustigman (1966) report that dinitrobenzenes are resistant to biodegradation by soil microorganisms. It has been reported that dinitrotoluenes are decomposed very slowly in a reservoir (Galuzova 1963). Biodegradation by *Azotobacter* has also been reported to be slow (Bringmann and Kuehn 1972).

82.5 Data Summary

Table 82-1 summarizes the aquatic fate discussed above for 2,6-dinitrotoluene. Intramolecular photolysis and, to a small extent, biodegradation may both be aquatic fates for this compound. Adsorption onto sediment probably plays a major role in transport and may also provide reaction sites for destruction. With the available data, however, it is not possible to determine which fate predominates.

Table 82-1

Summary of Aquatic Fate of 2,6-Dinitrotoluene

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis[a]	Probably responsible for color development in munition plant effluents.	-	-	High
Oxidation	Probably not important.	-	-	Low
Hydrolysis	Highly improbable based on the compound's resistance to electrophilic attack.	-	-	High
Volatilization	No specific data found; probably not important.	-	-	Medium
Sorption	Interaction with sediment highly probable with the possibility of stable complex formation.	-	-	Medium
Bioaccumulation	Importance not known.	-	-	Low
Biotransformation/ Biodegradation[a]	Slow but could be significant depending upon relative rates of other fate processes.	-	-	Low

---

a. Since intramolecular photolysis and biodegradation may both be aquatic fates for this compound, no predominant fate was assigned.

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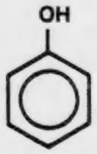
83. PHENOL

83.1 Statement of Probable Fate

Photooxidation, metal-catalyzed oxidation, and biodegradation probably all contribute to the fate of phenol in the aquatic environment. The dominance of any of these destructive pathways depends upon the particular environmental conditions of the aqueous medium but the degradation products are very similar for all fate pathways. The first step usually involves further hydroxylation of the aromatic ring followed by oxidation to a benzoquinone and cleavage of the ring structure. There is a possibility that some of the phenol that is present in surface waters volatilizes into the atmosphere and is rapidly destroyed by oxidation in the troposphere. Neither sorption nor bioaccumulation appear to be important processes in the aquatic fate of phenol.

83.2 Identification

Phenol has been detected in finished drinking water, surface waters, and industrial effluents (Shackelford and Keith 1976). The chemical structure of phenol is shown below.



Phenol

CAS NO. 108-95-2
TSL NO. SJ 33250

Alternate Names

Carbolic acid
Hydroxybenzene
Phenyl hydroxide
Phenic acid
Phenyl hydrate

83.3 Physical Properties

The general physical properties of phenol are as follows.

Molecular weight (Weast 1977)	94.11
Melting point (Andon _et al_. 1960)	40.90°C
Boiling point at 760 torr (Weast 1977)	181.75°C

Vapor pressure at 20°C (Andon et al. 1960)	0.5293 torr*
Solubility in water at 25°C (Morrison and Boyd 1973)	93,000 mg/l
Log octanol/water partition coefficient (McCall 1975)	1.46
pK_a (Herington and Kynaston 1957)	10.02

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*Vapor pressure of phenol as a supercooled liquid.

83.4 Summary of Fate Data

83.4.1 Photolysis

Phenol is a very weak acid, $pK_a = 10.02$ (Herington and Kynaston 1957), and exists principally as its protonated, non-ionized form in environmental surface waters. Coordination of the phenolic oxygen atom with dissolved or suspended di- and trivalent metal cations, however, can markedly increase the ionization of the phenolic proton. In the near ultraviolet spectral region the absorption maximum of undissociated phenol occurs at 270 nm and does not extend beyond 290 nm. The anion of phenol has an absorption maximum at 287 nm which extends to 310 nm (Herington and Kynaston 1957). Any environmental photolysis of phenol that could occur would, therefore, probably involve the phenolic anion or photosensitization of the undissociated form as an adsorbate. It should be noted that complexes of phenol with metal cations, such as iron (III), absorb light strongly at about 600 nm (Ackermann and Hesse 1970).

Solid or liquid phenol has long been known to form reddish high molecular weight material when exposed to sunlight and air (Joschek and Miller 1966). A possible explanation for these observations could be the formation and photolysis of an oxygen-phenol charge-transfer complex. Joschek and Miller (1966) report that the steady irradiation of aqueous solutions of phenol at 254 nm in the presence of oxygen yields isolable amounts of 4,4'-dihydroxybiphenyl, 2,4'-dihydroxybiphenyl, 2,2'-dihydroxybiphenyl, hydroquinone, and catechol as well as many uncharacterized compounds. The latter two compounds predominate as products in the more dilute solutions. The intermediate that is postulated to explain this distribution of products is the phenoxyl radical. If the phenoxyl radical can also be produced by irradiation of phenol under environmental conditions, it is expected that hydroquinone and catechol will be its main degradation products. In the presence of photosensitizers that can transfer their electronic excitation energy to molecular oxygen, the phenoxyl radical can react at the C-2 and C-4 positions with an excited triplet oxygen molecule to produce a phenoxylperoxy radical which decomposes directly to a 2- or 4-benzoquinone (Pfoertner and Böse 1970).

Environmentally relevant substantiation for photooxidative degradation has been reported by Perelshtein and Kaplin (1968) and Kinney and Ivanuski (1969). The former investigators used natural sunlight as a source of radiation, whereas the latter investigators used commercially available sun lamps. Both found a gradual reduction of aqueous phenol that could not be attributed to microbial degradation. Perelshtein and Kaplin (1968) proposed, on the basis of the ultraviolet absorption spectra of their solution samples, that hydroquinone was being synthesized from the phenol. The possible role of direct oxidation or volatilization in their experiments was not taken into account.

There is a possibility that volatilization of phenol will contribute to its removal from water (see Section 83.4.4). In the event that some phenol does evaporate with water into the atmosphere, it can be expected that rapid photooxidation will take place in the troposphere. Based upon the smog chamber studies of Altshuller _et al_. (1962) and Laity _et al_. (1973), the half-conversion times of m-xylene and toluene in a metropolitan airshed are about four hours and twelve hours, respectively. According to Laity _et al_. (1973) aromatic substituents that increase a molecule's susceptibility to electrophilic attack will increase its rate of photodestruction in the atmosphere. Inasmuch as the effect of a hydroxy group, in this regard, is much greater than that of a methyl group (Morrison and Boyd 1973), it can be assumed that any phenol which does get into the troposphere will be destroyed within a few hours.

83.4.2 Oxidation

Hydroxylation of aqueous phenol at the C-2 position in the presence of air and iron(III) or copper(II) ions has been reported but at temperatures and pressures far above what would be normally encountered in environmental surface waters (Makalets and Ivanova 1969). In addition, phenol has been oxidized by passing molecular oxygen into an aqueous solution at 25°C and pH 9.5-13 (Kirso _et al_. 1967). These observations, although not environmentally relevant in themselves, raise the possibility that phenol could be non-photolytically oxidized in highly aerated waters that also contained iron and copper in solution or as part of the suspended particulates.

83.4.3 Hydrolysis

There are no data to suggest that hydrolysis of phenol is an environmentally significant process. The covalent bond of a substituent attached to an aromatic ring is usually resistant to hydrolysis because of the high negative charge-density of the aromatic nucleus (Morrison and Boyd 1973).

83.4.4 Volatilization

The vapor pressure of supercooled liquid phenol at 20°C is 0.5293 torr at 20°C (Andon *et al.* 1960) and the solubility has been given as 93,000 mg/l (Morrison and Boyd 1973). A moderately low vapor pressure and a high solubility usually imply that there is little tendency for volatilization from water. Furthermore, it can be expected that aqueous phenol will be highly solvated which will increase its persistence in water at low levels of concentration. Nonetheless, it has been reported by Hakuta (1975) that the vapor-liquid distribution ratio of phenol in water at a concentration of 1 mg/l is 1.8 at atmospheric pressure, thus making volatilization from surface waters a distinct possibility. Moreover, when a thin layer of montmorillonite, that had been previously saturated with gaseous phenol, is exposed for one week to an atmosphere with a 40% relative humidity, the phenol becomes almost completely desorbed from the clay (Saltzman and Yariv 1975).

83.4.5 Sorption

Phenol has a log octanol/water partition coefficient of 1.46 (McCall 1975) and should, therefore, have only a slight tendency to become sorbed onto the organic detrius. Furthermore, phenol apparently would have very little affinity for microcrystalline clay particulates in the aquatic environment inasmuch as it can be almost completely desorbed from a thin layer of montmorillonite that has been exposed for one week to the atmosphere at 40% relative humidity (Saltzman and Yariv 1975). From the data of Chang and Anderson 1968, phenol also appears to be ineffective as a flocculant of clays and soils. This latter observation implies that phenol does not form stable organic-inorganic aggregates in an aqueous medium.

83.4.6 Bioaccumulation

The log octanol/water partition coefficient indicates that phenol should not be bioaccumulated to any extent in the aquatic environment. A review of the current literature revealed no information concerning the bioaccumulation of phenol by aquatic microorganisms or by aquatic invertebrates or vertebrates.

83.4.7 Biotransformation and Biodegradation

The microbial degradation of phenol has been observed in many laboratory studies in which phenol represented the primary carbon source provided for isolated and adapted microorganisms. Alexander and Lustigman (1966) observed that phenol was degraded rapidly by a mixed population of soil microorganisms. Their data suggested that the hydroxy group, compared to other benzene ring substituents, facilitated microbial degradation. Bayly et al. (1966) reported that Pseudomonas putida converted phenol to catechol. Buswell and Twomey (1975) and Buswell (1975) demonstrated the oxidation of phenol by thermophilic bacteria, Bacillus stearothermophilus. Other reports have documented the decomposition of phenol by yeasts, including strains belonging to the genera Oospora, Sacaromycetes, Candida, and Debaryomyces (Buswell 1975). Neujahr and Varga (1970) reported the oxidation of phenol by both intact cells and cell extracts of the yeast, Trichosporon cutaneum. The metabolic pathways involved in the microbial degradation of phenols have been well established (Neujahr and Varga 1970; Buswell 1975; and Buswell and Twomey 1975). The compound is first converted to catechol and the aromatic ring is subsequently cleaved to form 2-hydroxymuconic semialdehyde.

Happold and Key (1932) were among the first to demonstrate the bacterial degradation of phenol in phenolic wastes. Baird et al. (1974) examined the biodegradation of phenol under conditions simulating an aerobic biological sewage treatment system. At concentrations of 1 mg/l to 10 mg/l, phenol was biodegraded beyond the limits of detection. At a concentration of 100 mg/l, only 20% of the phenol was removed. At concentrations as low as 10 mg/l, however, phenol began to inhibit the oxygen uptake of the unacclimated sludge. These effects were greatly accentuated at 100 mg/l. With long acclimation periods, activated sludge can be conditioned to metabolize up to 500 mg/l phenol without exhibiting toxic effects (McKinney et al. 1956).

Biodegradation has been suggested as the mechanism for the decomposition of phenol in natural waters (Streeter 1929; Mischonsniky 1934; Krombach and Barthel 1964; Polisois et al. 1975; Wuhrmann 1972), and recent studies have examined the importance of microorganisms in this process. Visser et al. (1977) conducted an in situ investigation of the phenol-degrading activity of bacteria in river water. Phenol (125 μg/l) was added to containers holding large quantities of river water. The containers were incubated in the river along with sterilized controls. The removal rate of phenol was 30 μg/l per hour from the natural samples compared to < 1 μg/l per hour from the sterilized controls.

Increasing the aeration of a natural system appears to enhance the removal of phenol by microorganisms (Borighem and Vereecken 1978). Borighem and Vereecken (1978) found that the presence or absence of light had no influence on the biodegradation of phenol, but decreasing the concentration of phenol significantly reduced the lag time necessary to initiate degradation and increased the rates of removal.

In addition to aquatic microorganisms, the goldfish, Carrassius auratus, also is reported to be able to biotransform phenol. Kobayashi et al. (1976a) found phenol sulfate to be present in all organs, particularly the gallbladder. Biliary excretion was suggested as the mechanism of elimination in fish. This supposition appears to be supported by data obtained by Kobayashi *et al*. (1976b) who reported the *in situ* sulfate conjugation of phenol by liver tissue.

83.4.8 Other Reactions

Chlorophenols may be produced inadvertently by chlorination reactions which take place during the disinfection of wastewater effluents or drinking water sources. Phenol has been reported to be highly reactive to chlorine in dilute aqueous solutions over a considerable pH range (Carlson *et al*. 1975). The formation of 2- and 4-chlorophenol as well as more highly chlorinated phenols such as 2,4- and 2,6-dichlorophenol and 2,4,6-trichlorophenol has been reported under conditions similar to those employed during the disinfection of wastewater effluents (Aly 1968, Barnhart and Campbell 1972). The synthesis of 2-chlorophenol took place in 1 hour in aqueous solutions containing as little as 10 mg/l and 20 mg/l of phenol and chlorine, respectively (Barnhart and Campbell 1972).

83.5 Data Summary

Table 83-1 summarizes the aquatic fate data for phenol. Photooxidation, metal-catalyzed oxidation and biodegradation probably all contribute to the aquatic destruction of this pollutant. There is a possibility that some volatilization into the atmosphere can occur. Any phenol that passes into the atmosphere would be rapidly destroyed by oxidation in the troposphere. Neither sorption nor bioaccumulation appear to be important processes in the aquatic fate of phenol.

Table 83-1

Summary of Aquatic Fate of Phenol

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis[a]	Photooxidation may be an important degradative process in aerated clear surface waters.	-	-	Medium
Oxidation[a]	Metal-catalyzed oxidation may by relevant in some aerated surface waters.	-	-	Medium
Hydrolysis	Not a relevant environmental process.	-	-	High
Volatilization	There is a possibility of some phenol passing into the atmosphere.	-	-	Medium
Sorption	Not a significant process in the aquatic environment.	-	-	Medium
Bioaccumulation	Not a significant process in the aquatic environment.	-	-	Medium
Biotransformation/ Biodegradation[a]	A very significant fate pathway in aqueous media with a sufficient concentration of microorganisms.	-	-	High

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a. Photooxidation, metal-catalyzed oxidation and biodegradation are all probably relevant destructive fate pathways.

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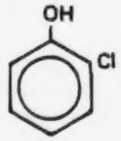
84. 2-CHLOROPHENOL

84.1 Statement of Probable Fate

From the information found in the reviewed literature, it is not possible to determine the most probable aquatic fate of this compound. Microbial degradation and photolysis have been demonstrated, but their environmental importance cannot be assessed from the available data. One or both of these processes probably would account for most of the degradation of 2-chlorophenol in an aqueous discharge. Other fate processes are probably not important for this compound. Similarly, the transport processes of volatilization and sorption do not appear to have an overbearing effect on removal of 2-chlorophenol.

84.2 Identification

2-Chlorophenol has been detected in finished drinking water and in industrial effluents (Shackelford and Keith 1976).



2-Chlorophenol

Alternate Names

o-Chlorophenol

CAS NO. 95-57-8
TSL NO. SK 26250

84.3 Physical Properties

The general physical properties of 2-chlorophenol are as follows.

Molecular weight (Verschueren 1977)	125.56
Melting point (Drahonovsky and Vacek 1971)	8.4°C
Boiling point at 760 torr (Verschueren 1977)	175.6°C
Vapor pressure at 20°C	2.2 torr (calculated)

Solubility in water at 20°C (Verschueren 1977)	28,500 mg/l
Log octanol/water partition coefficient (Leo *et al*. 1971)	2.17
pK_a (Drahonovsky and Vacek 1971)	8.52

84.4 Summary of Fate Data

84.4.1 Photolysis

2-Chlorophenol is a weak acid, $pk_a = 8.52$ (Drahonovsky and Vacek 1971), and will exist both as an anion and as an undissociated phenolic compound in environmental surface waters. The undissociated compound in cyclohexane does not absorb electromagnetic radiation above 290 nm (Sadtler Standard Spectra 1975). In aqueous solution, however, the anion has an absorption maximum at 293 nm that extends beyond 310 nm (Drahonovsky and Vacek 1971). It also should be noted that the aqueous iron(III) complex of 2-chlorophenol has an absorption maximum at 550 nm (Ackermann and Hesse 1970).

It is uncertain whether the reported photolytic experiments on 2-chlorophenol can be extrapolated for interpretation within an environmental context. Grabowski (1961) has reported that the photolysis of 2-chlorophenol in aqueous alkali at 313 nm results in the replacement of chlorine by a hydroxy group. Omura and Matsuura (1971) found that irradiation of 2-chlorophenol in aqueous alkali produced intractable tars both at 254 nm and above 290 nm. Although it is obvious that it is the anion of 2-chlorophenol that is undergoing photolysis, it is not clear whether the resulting intermediate reacts with water or hydroxide ion. Omura and Matsuura (1971) were able to demonstrate with 4-chlorophenol that when cyanide ion was present in the photolysis solutions, some of the substituent chlorine was replaced by cyano groups. This latter observation supports a reaction mechanism involving anion interaction with the photolyzing carbon-chlorine bond. Based on the results of these experiments, the anion of 2-chlorophenol should be capable of undergoing photolysis within the environment of ambient surface waters but it is not clear what the resulting products would be.

It is not known whether 2-chlorophenol can volatilize from water into the atmosphere. In the event that some of this compound should evaporate with water into the troposphere, it probably will undergo photodegradation. The atmospheric half-life of benzene, proposed by Darnall *et al*. (1976), is 2.4 to 24 hours. According to Laity *et al*. (1973), a chlorine substituent on benzene should decrease its susceptibility to photodegradation in the troposphere while a hydroxy group should facilitate destruction. What effect the presence of both groups would have on the atmospheric destruction of the aromatic ring is unknown.

84.4.2 Oxidation

Günther *et al.* (1971) have demonstrated that hydroxyl radicals attack 2-chlorophenol at the C-2 and C-4 positions resulting in the formation of a complex mixture. No information was found, however, from which an environmentally relevant rate could be estimated for this reaction.

84.4.3 Hydrolysis

There are no data to suggest that hydrolysis of 2-chlorophenol is an environmentally significant process. The covalent bond of a substituent attached to an aromatic ring is usually resistant to hydrolysis because of the high negative charge-density of the aromatic nucleus (Morrison and Boyd 1973).

84.4.4 Volatilization

The calculated vapor pressure of 2-chlorophenol, 2.2 torr at 20°C, is moderate and thus volatilization could be a potential transport process for removal of this pollutant from surface waters. The high solubility, 28,500 mg/l, of 2-chlorophenol, however, would increase its resistance to volatilization at low concentrations in water. Furthermore, acidic substances are usually highly solvated. No specific data on the rate of volatilization of 2-chlorophenol was found although it is surmised that volatilization is not a competing removal process.

84.4.5 Sorption

The value of the log octanol/water partition coefficient (log $P=2.17$) indicates a slight potential for sorption by lipophilic materials in the sediment and particulates. The only specific study of adsorption to soils of a chlorinated phenol appears in Aly and Faust (1964). Sorption of 2,4-dichlorophenol to kaolinite, Wyoming bentonite (a montmorillonitic clay), and Fithian illite was measured. Sorption to illite and bentonite, which are more negatively charged than kaolinite, was considerably greater than to the latter. Bentonite has a larger specific surface area than the other clays, and the order of decreasing sorption (bentonite, illite, kaolinite) correlates with decreasing specific surface area. The essential conclusion is that sorption to sedimentary clays or suspended clays in surface waters will not remove significant amounts of chlorinated phenols.

84.4.6 Bioaccumulation

No information concerning the bioaccumulation of 2-chlorophenol in aquatic plants or animals was found. Spencer and Williams (1950) investigated the fate of oral doses of 2-chlorophenol administered to rabbits. The results indicated that urinary excretion was rapid and probably represents the major route of elimination from mammals. As a group, the chlorophenols (2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, and pentachlorophenol) are more likely to bioaccumulate as the number of attached chlorine groups increases (Alexander and Aleem 1961).

84.4.7 Biotransformation and Biodegradation

In general, chlorophenols are more stable to biodegradation than phenol, and resistance to microbial catabolism is greatest among the more highly chlorinated phenols (Alexander and Aleem 1961). Information found in the reviewed literature on the biodegradability of 2-chlorophenol is limited to laboratory studies. At low concentrations (1-10 ppm) 2-chlorophenol is completely degraded by pure and mixed cultures of bacteria after 3-6 hours (Baird *et al*. 1974; Loos *et al*. 1967). At 100 ppm, however, only 20% of it is degraded (Baird *et al*. 1974). 2-Chlorophenol is probably degraded by co-metabolism, although it does support the growth of common aquatic bacteria (Knackmuss and Hellwig, 1978). Natchtigall and Butler (1974) report the microbial degradation of 2-chlorophenol by several species of *Pseudomonas* and a species of *Arthrobacter*, all isolated from various soils. The extrapolation of these laboratory conditions to environmental situations may have very limited value. Verschueren (1977) reports: (a) a decomposition rate of 14 days for complete disappearance of 2-chlorophenol in a soil suspension, and (b) a decomposition period by soil microflora of over 64 days.

No studies were found that discussed what minimum levels of the pollutant are required to induce catabolic pathways. It is reasonable to suppose that genetic induction levels for most degradative organisms will not be reached except in the vicinity of discharges. Thus, stagnant receiving waters with stable, high levels of chlorinated phenols may establish and maintain a degradative microflora able quickly to degrade the pollutant, provided oxygen is not limiting. Rapid dilution in fast-flowing receiving waters, on the contrary, will make establishment of an adapted microflora much less likely and biodegradation should be slower, even with greater aeration.

84.4.8 Other Reactions

Chlorophenols may be produced inadvertently by chlorination reactions which take place during the disinfection of wastewater effluents or drinking water sources. Unsubstituted phenol has been reported to be highly reactive to chlorine in dilute aqueous solutions over a considerable pH range (Carlson et al. 1975). The formation of 2- and 4-chlorophenol as well as more highly chlorinated phenols such as 2,4- and 2,6-dichlorophenol and 2,4,6-trichlorophenol has been reported under conditions similar to those employed during the disinfection of wastewater effluents (Aly 1968; Barnhart and Campbell 1972). 2-Chlorophenol can serve as an intermediate in the synthesis of the more highly chlorinated phenols (Morrison and Boyd 1973).

84.5 Data Summary

Table 84-1 summarizes the aquatic fate data for 2-chlorophenol. Microbial degradation has been well substantiated but the rates are dependent on numerous variables. Photolysis also has been demonstrated but its significance in the environment is uncertain. Other fate processes probably do not compete to any signficant extent. The transport processes of volatilization and adsorption probably do not have an overbearing effect on the removal of this pollutant.

Table 84-1

Summary of Aquatic Fate of 2-Chlorophenol

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis[a]	Photolysis has been reported but its environmental importance is uncertain.	-	-	Low
Oxidation	Not considered to be an important process.	-	-	Low
Hydrolysis	No information found; is thought not to be an important process.	-	-	Low
Volatilization	Probably does not have an overbearing consequence on the aquatic fate.	-	-	Low
Sorption	No specific information found; probably not important.	-	-	Low
Bioaccumulation	Probably not bioaccumulated; log P = 2.17.	-	-	Low
Biotransformation/ Biodegradation[a]	Microbial degradation has been reported; the environmental rate is uncertain.	-	-	Low

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a. Both photolysis and microbial degradation have been demonstrated but their relative importance in the environment with respect to each other is uncertain.

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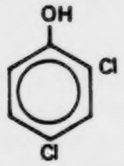
85. 2,4-DICHLOROPHENOL

85.1 Statement of Probable Fate

2,4-Dichlorophenol is readily biodegraded and probably does not bioaccumulate in the aquatic environment. Although photolysis of 2,4-dichlorophenol in the presence of a photosensitizer has been reported to occur, the rate of photolysis has been observed to be slower than the rate of microbial degradation. Neither oxidation nor hydrolysis contributes significantly to the aquatic fate of this pollutant, and neither volatilization nor sorption is considered to be important in its transport.

85.2 Identification

2,4-Dichlorophenol (2,4-DCP) has been detected in municipal and industrial effluents, finished drinking water, and surface waters (Shackelford and Keith 1976). The chemical structure is shown below.



Alternate Name

2,4-DCP

2,4-Dichlorophenol

CAS NO. 120-83-2
TSL NO. SK 85750

85.3 Physical Properties

The general physical properties of 2,4-dichlorophenol are as follows.

Molecular weight (Verschueren 1977)	163.0
Melting point (Verschueren 1977)	45°C
Boiling point at 760 torr (Verschueren 1977)	210°C
Vapor pressure at 20°C	0.12 torr (calculated)

Solubility in water at 20°C (Verschueren 1977)	4500 mg/l
Log octanol water/partition coefficient (Tute 1971)	2.75
pK_a (Pearce and Simkins 1968)	7.85

85.4 Summary of Fate Data

85.4.1 Photolysis

Crosby and Tutass (1966) have reported the photodegradation of aqueous 2,4-dichlorophenol when it is exposed to near ultraviolet or solar radiation under conditions of good aeration. After 10 days of solar irradiation, 2,4-dichlorophenol could no longer be detected in the solution and most of it appeared to have been converted to an insoluble dark acidic tarry substance. Crosby and Tutass (1966) proposed that the tarry substance was formed by the polymerization of 2-hydroxybenzoquinone, an oxidation product of 1,2,4-benzenetriol which results from the photolysis of the carbon-chlorine bonds.

Plimmer et al. (1971), however, found that irradation of 2,4-dichlorophenol with light at wavelengths above 280 nm induced a negligible amount of photolysis. No photoreaction was observed without the presence of a photosensitizer, such as riboflavin. The reaction products from 2,4-dichlorophenol, in the presence of riboflavin, were a mixture of tetrachlorophenoxyphenols and tetrachlorodihydroxybiphenyls. None of the highly toxic chlorinated dibenzodioxins could be detected. Despite extensive destruction of the 2,4-dichlorophenol, its conversion to dimeric products was less than 5%.

In a study of microbial degradation of this pollutant in samples of natural lake water, Aly and Faust (1964) observed that photolysis was insignificant compared to microbial catabolism.

85.4.2 Oxidation

Günther et al. (1971) have demonstrated that hydroxyl radicals attack 2-chlorophenol at the C-2 and C-4 positions resulting in the formation of a complex mixture. No information was found, however, from which an environmentally relevant rate could be estimated for this reaction. It can be inferred that 2,4-dichlorophenol could also undergo reactions of this type but at a much slower rate (Morrison and Boyd 1973).

85.4.3 Hydrolysis

There are no data to suggest that hydrolysis of 2,4-dichlorophenol is an environmentally significant process. The covalent bond of a substituent attached to an aromatic ring is usually resistant to hydrolysis because of the high negative charge-density of the aromatic nucleus (Morrison and Boyd 1973).

85.4.4 Volatilization

Compounds with a moderate solubility (4500 mg/l) and a low vapor pressure (0.12 torr at 20°C) generally do not volatilize from water. Furthermore, 2,4-dichlorophenol is a weak acid ($pK_a = 7.85$; Pearce and Simkins 1968) and will be about 50 percent ionized and very surely solvated in environmental surface waters.

85.4.5 Sorption

The value of the log octanol/water partition coefficient (P=2.75) indicates a slight potential for sorption by lipophilic materials in the sediment and particulates. The only specific study of 2,4-dichlorophenol adsorption by soils appears in Aly and Faust (1964). Sorption to kaolinite, Wyoming bentonite (a montmorillonitic clay), and Fithian illite was measured. Sorption to illite and bentonite, which are more negatively charged than kaolinite, was considerably greater than to the latter. Bentonite has a larger specific surface area than the other clays, and the order of decreasing sorption (bentonite, illite, kaolinite) correlates with decreasing specific surface area. The essential conclusion is that sorption to sedimentary clays or suspended clays in surface waters will not remove significant amounts of 2,4-dichlorophenol.

85.4.6 Bioaccumulation

Little information exists concerning the bioaccumulation of 2,4-dichlorophenol. Isensee and Jones (1971), using ^{14}C-labelled 2,4-dichlorophenol, demonstrated that oats and soybean seedlings concentrated 2,4-dichlorophenol from dilute solutions (0.2 mg/l) by factors of 9.2X for oats and 0.65X for soybean. No further concentration took place during the remaining 13 days of the experiment. As a group, the chlorophenols are more likely to bioaccumulate as the number of attached chlorine groups increase.

85.4.7 Biotransformation and Biodegradation

Microbial decomposition of 2,4-dichlorophenol has been studied extensively in connection with work on the herbicide 2,4-D (2,4-dichlorophenoxyacetic acid). Alexander and Aleem (1961) claimed complete disappearance of 2,4-dichlorophenol in 5 or 9 days in two different silt loam suspensions when the initial concentration was 50 mg/l. Aly and Faust (1964) studied 2,4-dichlorophenol oxidative degradation in samples of natural lake water under laboratory conditions (pH 7, aeration, 25°C). An initial concentration of 100 μg/l was completely eliminated in 9 days. Concentrations of 500 and 1000 μg/l were 97.5 percent eliminated in 30 days. The half-life of 2,4-dichlorophenol in their cultures was 6 days. Adaptation of the cultures was apparently unnecessary and photolysis was not rapid enough to be competitive. (It should be noted that these observations could also be explained by the volatilization of this pollutant.) In a lake water culture simulating eutrophic conditions, the 2,4-dichlorophenol was much more persistent with significant levels remaining after 43 days. The eutrophic cultures showed hydrogen sulfide generation and a drop in pH. In a non-aquatic rate study, Macrae *et al.* (1963) found that a soil bacterium (*Flavobacterium sp.*) adapted to 2,4-D butyl ester was able to completely oxidize 163 μg/l of 2,4-dichlorophenol in 60 minutes.

Soil bacteria that have been shown to carry out 2,4-dichlorophenol oxidation include *Pseudomonas*, *Achromobacter*, *Arthrobacter*, *Flavobacterium*, and mixed soil cultures (Alexander and Aleem 1961; Macrae *et al.* 1963; Paris and Lewis 1973; Bollag *et al.* 1968; Chu and Kirsch 1972; Ingols *et al.* 1966; Loos *et al.* 1967; Tiedje *et al.* 1969). Loos *et al.* (1967) found that *Arthrobacter* could methylate 2,4-dichlorophenol to form 2,4-dichloroanisole. The significance of this chlorinated anisole as a biotransformation product has not been explored. Chu and Kirsch (1972) showed that an unidentified bacillus soil culture adapted to pentachlorophenol was also readily able to degrade 2,4-dichlorophenol. The dichlorophenol was 67 percent oxidized by a suspension of the bacillus in 150 min. Ingols *et al.* (1966) also observed 2,4-dichlorophenol degradation by pentachlorophenol-adapted sludge.

No studies of induction kinetics or of metabolic interactions in mixed cultures were found in the reviewed literature. Similarly, no studies were found that discussed what minimum levels of the pollutant are required to induce catabolic pathways. It is reasonable to suppose that genetic induction levels for most degradative organisms will not be reached except in the vicinity of discharges. Thus, stagnant receiving waters with stable, high levels of 2,4-dichlorophenol will establish and maintain a degradative microflora able quickly to degrade the pollutant, provided oxygen is not limiting. Rapid dilution in fast-flowing receiving waters, on the contrary, will make establishment of an adapted microflora much less likely and biodegradation should be slower, even with greater aeration.

85.4.8 Other Reactions

Chlorophenols may be produced inadvertently by chlorination reactions which take place during the disinfection of wastewater effluents or drinking water sources. Unsubstituted phenol has been reported to be highly reactive to chlorine in dilute aqueous solutions over a considerable pH range (Carlson *et al*. 1975). The formation of 2- and 4-chlorophenol as well as more highly chlorinated phenols such as 2,4- and 2,6-dichlorophenol and 2,4,6-trichlorophenol has been reported under conditions similar to those employed during the disinfection of wastewater effluents (Aly 1968; Barnhart and Campbell 1972). 2 4-Dichlorophenol can serve as an intermediate in the synthesis of 2,4,6-trichlorophenol (Morrison and Boyd 1973).

85.5 Data Summary

Table 85-1 summarizes the aquatic fate data for 2,4-dichlorophenol. Microbial degradation has been well substantiated but the rates are dependent on numerous variables. Other fate processes probably do not compete to any significant extent. The transport processes of volatilization and adsorption probably do not have an overbearing effect on the removal of this pollutant.

Table 85-1

Summary of Aquatic Fate of 2,4-Dichlorophenol

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Photolysis probably does not significantly compete with microbial biodegradation.	-	-	Low
Oxidation	Not thought to be an important process.	-	-	Low
Hydrolysis	Not thought to be an important process.	-	-	Low
Volatilization	Not considered to be a significant transport process, although no specific data were found.	-	-	Low
Sorption	Not considered to be a significant transport process.	-	-	Low
Biotransformation/ Biodegradation	Probably not important in the aquatic environment although little supportive information was found.	-	-	Low
Biotransformation/ Biodegradation [a]	Microbial degradation has been well substantiated; rates are dependent on numerous variables.	-	6 days [b]	Medium

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a. The predominant environmental process which is thought to determine the fate of the compound.

b. This half-life is for well aerated samples of lake water and should be considered as a minimum half-life (Aly and Faust 1964).

85.6 Literature Cited

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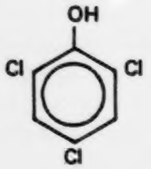
86. 2,4,6-TRICHLOROPHENOL

86.1 Statement of Probable Fate

From the information that was found in the reviewed literature, it is not possible to determine the most probable aquatic fate of this pollutant. Microbial degradation and photolysis have been demonstrated, and, although their significance in surface waters is uncertain, one or both of these processes probably would account for most of the degradation of environmental 2,4,6-trichlorophenol. Other fate processes are probably not relevant to the aquatic environment. Similarly, the transport process of volatilization probably does not have an overbearing effect on the removal of 2,4,6-trichlorophenol. Based on the log octanol/water partition coefficient, there is a definite potential for sorption by organic matter.

86.2 Identification

2,4,6-Trichlorophenol has been detected in finished drinking water (Shackelford and Keith 1976). The chemical structure is shown below.



2,4,6-Trichlorophenol

CAS NO. 88-06-2
TSL NO. SN 15750

Alternate Names

No data found

86.3 Physical Properties

The general physical properties of 2,4,6-trichlorophenol are as follows.

Molecular weight (Verschueren 1977)	197.45
Melting point (Verschueren 1977)	68°C
Boiling point at 760 torr (Verschueren 1977)	244.5°C
Vapor pressure at 76.5°C (Verschueren 1977)	1 torr

Solubility in water at 25°C (Verschueren 1977)	800 mg/l
Log octanol/water partition coefficient (Leo *et al*. 1971)	3.38
pK_a (Drahonovsky and Vacek 1971)	5.99

86.4 Summary of Fate Data

86.4.1 Photolysis

2,4,6-Trichlorophenol is a moderately acidic substance, pK_a = 5.99 (Drahonovsky and Vacek 1971), and will exist substantially as an anion in environmental surface waters. The ultraviolet absorption spectrum of the anion exhibits a maximum absorption peak at 311 nm while the undissociated form has an absorption maximum at 286 nm (Drahonovsky and Vacek 1971). It also should be noted that the iron(III) complex of 2,4,6-trichlorophenol has an absorption maximum at 570 nm (Ackermann and Hesse 1970).

In the presence of an electron acceptor, 2,4,6-trichlorophenol can be photooxidized to 2,6-dichlorophenoxyl semiquinone radical anion (Leaver 1971). The semiquinones thus formed disproportionate rapidly to 2,6-dichlorobenzoquinone and 2,6-dichlorohydroquinone. No further information which specifically pertained to the photolysis of 2,4,6-trichlorophenol was found in the reviewed literature.

The experimental photolysis of 2,4-dichlorophenol, however, has been described. For example, Crosby and Tutass (1966) have reported the photodegradation of aqueous 2,4-dichlorophenol when it is exposed to near ultraviolet or solar radiation under conditions of good aeration. After 10 days of solar irradiation, 2,4-dichlorophenol could no longer be detected in the solution and most of it appeared to have been converted to an insoluble dark acidic tarry substance. Crosby and Tutass (1966) proposed that the tarry substance was formed by the polymerization of 2-hydroxybenzoquinone, an oxidation product of 1,2,4-benzenetriol which results from the photolysis of the carbon-chlorine bonds.

In contrast, Plimmer *et al*. (1971) found that irradiation of 2,4-dichlorophenol with light at wavelengths above 280 nm induced a negligible amount of photolysis. No photoreaction was observed without the presence of a photosensitizer, such as riboflavin. The reaction products from 2,4-dichlorophenol, in the presence of riboflavin, were a mixture of tetrachlorophenoxyphenols and tetrachlorodihydroxybiphenyls. In a study of the microbial degradation of 2,4-dichlorophenol in samples of natural lake water, Aly and Faust (1964) reported that photolysis was insignificant compared to microbial catabolism. It is uncertain to what extent these reported photolytic experiments on 2,4-dichlorophenol can be extrapolated to 2,4,6-trichlorophenol for interpretation within an environmental context.

86.4.2 Oxidation

Günther et al. (1971) have demonstrated that hydroxyl radicals attack 2-chlorophenol at the C-2 and C-4 positions resulting in the formation of a complex mixture. No information was found, however, from which an environmentally relevant rate could be estimated for this reaction. It can be inferred that 2,4,6-trichlorophenol might also undergo reactions of this type but at a much slower rate (Morrison and Boyd 1973).

86.4.3 Hydrolysis

There are no data to suggest that the hydrolysis of 2,4,6-trichlorophenol is an environmentally relevant process. The covalent bond of a substituent attached to an aromatic ring is resistant to hydrolysis because of the high negative charge-density of the aromatic nucleus (Morrison and Boyd 1973).

86.4.4 Volatilization

Compounds with an appreciable solubility (800 mg/l) and a low vapor pressure (1 torr at 76.5°C) generally do not volatilize from water. Furthermore, 2,4,6-trichlorophenol is a moderately acidic substance (pk_a = 5.99; Drahonovsky and Vacek 1971) and will be substantially ionized and very surely solvated in environmental surface waters.

86.4.5 Sorption

The value of the log octanol/water partition coefficient (3.38) indicates a definite potential for sorption by lipophilic materials in the sediment and particulates. The only specific study of adsorption to soils of a chlorinated phenol appears in Aly and Faust (1964). Sorption of 2,4-dichlorophenol to kaolinite, Wyoming bentonite (a montmorillonitic clay), and Fithian illite was measured. Sorption to illite and bentonite, which are more negatively charged than kaolinite, was considerably greater than to the latter. Bentonite has a larger specific surface area than the other clays, and the order of decreasing sorption (bentonite, illite, and kaolinite) correlates with decreasing specific surface area. The essential conclusion is that sorption to sedimentary clays in surface waters will not move significant amounts of chlorinated phenols. Sorption by the organic detritus, however, may be important.

86.4.6 Bioaccumulation

No information was found concerning the bioaccumulation of 2,4,6-trichlorophenol. Isensee and Jones (1971), using ^{14}C-labelled 2,4-dichlorophenol demonstrated that oats and soybean seedlings were able to concentrate it from dilute solutions (0.2 mg/l) by factors of 9.2x for oats and 0.65x for soybean. No further concentration took place during the remaining 13 days of the experiment. As a group, the chlorophenols are more likely to become bioaccumulated as the number of attached chlorine atoms increases.

86.4.7 Biotransformation and Biodegradation

Limited published information was found in the reviewed literature on biodegradation of 2,4,6-trichlorophenol. In flask cultures inocculated with sludge bacteria, 7-10 days were required to remove 95% of the 2,4,6-trichlorophenol at an initial concentration of 300 ppm (Tabak *et al.* 1964). At lower concentrations (100 ppm) respirometry experiments indicated that 70% of the 2,4,6-trichlorophenol can be removed in 3 hours (Tabak *et al.* 1964). In soil cultures 5-13 days were required for complete removal of 2,4,6-trichlorophenol. Alexander and Aleem (1961) found in their experiments that the time required for the complete disappearance of some chlorophenols, including 2,4,6-trichlorophenol from various soil samples ranged from 1 to 9 days. Ingols *et al.* (1966) reported complete aromatic ring degradation of 2,4,6-trichlorophenol within 5 days by microbial action in an acclimated sludge. Thus, it appears that 2,4,6-trichlorophenol is susceptible to biodegradation but its fate *in situ* in aquatic systems remains uncertain.

No studies of induction kinetics or of metabolic interactions in mixed cultures were found in the reviewed literature. Similarly, no studies were found that discussed what minimum levels of the pollutant are required to induce catabolic pathways. It is reasonable to suppose that genetic induction levels for most degradative organisms will not be reached except in the vicinity of discharges. Thus, stagnant receiving waters with stable, high levels of 2,4,6-trichlorophenol will establish and maintain a degradative microflora able quickly to degrade the pollutant, provided oxygen is not limiting. Rapid dilution in fast-flowing receiving waters, on the contrary, will make establishment of an adapted microflora much less likely and biodegradation could, under these circumstances, be insignificant.

86.5 Data Summary

Table 86-1 summarizes the aquatic fate for 2,4,6-trichlorophenol. Microbial degradation has been demonstrated but the rates are dependent on numerous variables. Photolysis also has been demonstrated but its significance in the environment is uncertain. Other fate processes probably do not compete to any relevant extent. The transport process of volatilization probably does not have an overbearing effect on the removal of this pollutant, but sorption by organic matter may be important.

Table 86-1

Summary of Aquatic Fate of 2,4,6-Trichlorophenol

Environmental Process[a]	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Photolysis has been reported but the environmental relevance is uncertain.	-	-	Low
Oxidation	Thought not to be a competitive process in the aquatic environment.	-	-	Low
Hydrolysis	Not thought to be an environmentally relevant process.	-	-	Low
Volatilization	Probably not significant in the aquatic environment.	-	-	Low
Sorption	The log octanol/water partion coefficient (3.38) indicates a definite potential for sorption by organic material. Adsorption by clays is probably unimportant.	-	-	Low
Bioaccumulation	No specific information found; probably not important.	-	-	Low
Biotransformation/ Biodegradation	Biodegradation has been demonstrated in soil samples and in acclimated sewage sludge but it is uncertain as a process in ambient surface waters.	-	-	Low

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

86.6 Literature Cited

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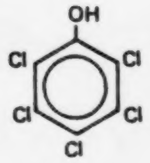
87. PENTACHLOROPHENOL

87.1 Statement of Probable Fate

Both photolysis and biodegradation appear to be important fate processes in the aquatic environment for pentachlorophenol. Photolytic destruction is probably rapid near the water-surface but as depth increases microbial metabolism assumes greater importance. Photolysis leads to a mixture of chloranilic acid, chlorinated phenols, chlorinated dihydroxybenzenes and smaller non-aromatic compounds. Microbial metabolism produces pentachloroanisole and a mixture of chlorinated phenols. Pentachlorophenol is accumulated by a large number of aquatic organisms and, in some cases, appears to be bioconcentrated. Although detoxification and depuration involving formation of a sulfate ester conjugate has been demonstrated in fish, the accumulation of pentachloroanisole in the fish of a natural aquatic environment has also been documented. Sorption by the organic matter of sediments and soil definitely plays a role in the storage and transport of this pollutant. In a study of a natural freshwater lake, leaf litter and other organic matter in the soil and sediments of the lake's watershed retained relatively high concentrations of pentachlorophenol and its degradation products, and this served as a source for continual pollution of the aquatic ecosystem. Hydrolysis, oxidation, and volatilization do not appear to affect the environmental fate of pentachlorophenol.

87.2 Identification

Pentachlorophenol has been detected in drinking water, rainwater, surface waters and effluents (Bevenue et al. 1972; Fountaine et al. 1976; Pierce and Victor 1978; Rudling 1970; Shackelford and Keith 1976). The chemical structure is shown below.



Pentachlorophenol

CAS NO. 87-86-5
TSL NO. SM 63000

Alternate Names

PCP
Chlorophen
Penchlorol

87.3 Physical Properties

The general physical properties of pentachlorophenol are given below.

Molecular weight (Verschueren 1977)	266.35
Melting point (Verschueren 1977)	190°C
Boiling point at 760 torr (Verschueren 1977)	310°C
Vapor pressure at 20°C (Bevenue and Beckman 1967)	0.00011 torr
Solubility in water at 20°C (Verschueren 1977)	14 mg/1*
Log octanol/water partition coefficient (Leo *et al*. 1971)	5.01
pK_a (Drahonovsky and Vacek 1971)	4.74

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*Windholz (1976) lists the solubility as 80 mg/l. In a natural water system this pollutant will be present primarily as an anion and its solubility, therefore, will be dependent on the cationic composition of the water. The anion, however, will be much more soluble than the undissociated compound under any circumstances.

87.4 Summary of Fate Data

87.4.1 Photolysis

Pentachlorophenol (PCP) is a moderately acidic substance, pk_a = 4.74 (Drahonovsky and Vacek 1971), and will exist primarily as an anion in environmental surface waters. The ultraviolet absorption spectrum of pentachlorophenol in dilute aqueous solutions at pH 7 has major absorption peaks at 245 nm and 318 nm (Hiatt *et al*. 1960). This is essentially the absorption spectrum of the anion (Drahonovsky and Vacek 1971).

Kuwahara *et al*. (1966 ab) found that a 2% solution of the sodium salt of pentachlorophenol was degraded to the extent of 50% when exposed to sunlight for ten days. The major products were identified as chloranilic acid (2,5-dichloro-3,6-dihydroxybenzoquinone), tetrachlororesorcinol, and several complex chlorinated benzoquinones. Hiatt et al. (1960) calculated the rate constant for the aqueous photochemical degradation of sodium pentachlorophenolate at an initial concentration of 10 mg/l and with a light intensity of approximately 0.04 watts/cm^2 between 290 and 330 nm. A first-order plot was obtained with $k = 3.4 \times 10^{-4}$ sec^{-1}. Using this value to estimate the rates of destruction of sodium pentachlorophenolate at various depths at noontime in a clear body of water on a midsummer day at the latitude of Cleveland, Ohio, the approximate half-lives at 10 cm and 300 cm were 0.2 hr and 4.75 hr, respectively.

Wong and Crosby (1978) found that the rate of photolysis of pentachlorophenolate anion was much faster than that of the undissociated compound. At pH 7.3 degradation of pentachlorophenol at a concentration of 100 mg/l was achieved within five to seven days by sunlight during the summer months in Davis, California whereas at pH 3.3 photolysis was much slower. From the data of Wong and Crosby (1978) an approximate half-life for aqueous photolysis at Davis, California can be estimated as 1.5 days during the summer months. When the irradiation was interrupted at a point where 50 to 75% of the pentachlorophenol had been degraded, three types of degradation products were isolated: chlorinated phenols, chlorinated dihydroxybenzenes, and non-aromatic fragments. The chlorinated phenols were reported to consist primarily of 2,3,4,6- and 2,3,5,6-tetrachlorophenol together with a mixture of trichlorophenols. Tetrachlororesorcinol and tetrachlorocatechol were isolated but tetrachlorohydroquinone was considered to be too unstable for isolation and probably was the main precursor for the principal non-aromatic degradation product, dichloromaleic acid. Plimmer et al. (1971) and Stehl et al. (1971) report that octachlorodibenzo-p-dioxin is produced in trace amounts during the photolysis of pentachlorophenolate anion.

Pierce and Victor (1978) monitored the fate of pentachlorophenol and its degradation products that had been introduced into a freshwater lake from an accidental release of wood-treating wastes which had been held in a settling pond. The origin of two of the major degradation products, 2,3,5,6- and 2,3,4,5-tetrachlorophenol was attributed to photolytic dechlorination of pentachlorophenol while it was still being held in the settling pond along with hydrocarbon wastes.

87.4.2 Oxidation

Although no specific information was found pertaining to the oxidation of pentachlorophenol, highly chlorinated organic compounds are usually resistant to oxidation even at temperature extremes that could not be reached in the aquatic environment (Morrison and Boyd 1973). Therefore, oxidation would not be expected to be an important fate under ambient conditions.

87.4.3 Hydrolysis

The covalent bond of a substituent attached to an aromatic ring is usually resistant to hydrolysis because of the high negative charge-density of the aromatic nucleus. For example, the synthesis of pentachlorophenolate anion from hexachlorobenzene requires treatment of the hexachlorobenzene with concentrated alkali at 130-200°C (Leoni and D'Arca 1976). It can be assumed that more extreme conditions would be necessary for further hydrolysis of the pentachlorophenolate anion. Therefore, hydrolysis is not a relevant fate for this pollutant.

87.4.4 Volatilization

Compounds with a moderate solubility in water and a very low vapor pressure generally do not volatilize from water. Furthermore, pentachlorophenol is a moderately acidic substance and will be substantially ionized and very surely solvated. Volatilization, therefore, is not considered to be an operative transport process.

87.4.5 Sorption

The data of Hiatt et al. (1960) indicate that sorption of pentachlorophenol occurs principally on acidic soil systems with little or no adsorption occurring on neutral soils. Choi and Aomine (1974) have reported that pH is the most important variable in controlling the adsorption of pentachlorophenol onto soils and that the actual amount of sorption is directly related to the organic content of the soil. Based on these data and the values of the pk_a and the log octanol/water partition coefficient ($pk_a = 4.74$; $\log P = 5.01$), sorption of dissolved pentachlorophenol by suspended organic particulates in circumneutral water would not be expected to occur. Organic rich sediments that become somewhat acidic due to anaerobic microbial digestion products could, however, be capable of sorbing substantial amounts of pentachlorophenol.

The observations of Pierce (1978) and Pierce and Victor (1978) on the fate of two accidental spills of pentachlorophenol into a freshwater lake have borne out these expectations. Sediments and leaf litter retained high concentrations of pentachlorophenol and its degradation products throughout the period that the lake was monitored, and thus provided a source for continuing pollution of the aquatic ecosystem. Furthermore, rainfall produced a chronic influx of pentachlorophenol by either leaching of the contaminated soil in the watershed area or by transporting leaf litter into the lake. Thus, sorption by the organic material of soil and sediments apparently plays an important role in the storage and transport of this pollutant.

87.4.6 Bioaccumulation

The log octanol/water partition coefficient indicates that pentachlorophenol (PCP) should be bioaccumulated significantly in the aquatic environment. This supposition seems to be supported by data obtained in a number of laboratory studies. Weinbach and Nolan (1956) observed a 33-fold and 50-fold concentration of pentachlorophenol in a species of snail after 24 and 30 hours, respectively, in a solution that contained 2 mg/l of the compound. Guppies, (Lebistes reticulatus), killed by lethal doses of pentachlorophenol within 18 hours, were found to contain approximately 100 μg PCP/g wet weight of tissue (Stark 1969).

The Japanese littleneck clam (Tapes phillipinarum) has also been reported to accumulate pentachlorophenol (Kobayashi *et al*. 1970). Seidel (1974) observed that the compound can be absorbed from water by two species of marsh plants, soft rush (Juncus effusus L.) and sea rush (J. maritimis L.).

Akitake and Kobayashi (1975) demonstrated that a 72-hour exposure to a sublethal level of pentachlorophenol of 100 μg/l resulted in a 900-fold concentration of the compound in the goldfish, Carassius auratus. In another study (Kobayashi and Akitake 1975), these authors investigated the absorption at three concentrations (0.1, 0.2 and 0.4 mg/l) of pentachlorophenol by goldfish and found that the amount accumulated by the fish increased with time. They reported a concentration factor of 1000 after exposure for 120 hr. in 0.1 mg/l pentachlorophenol and observed a maximum concentration of 116 μg PCP/g body weight in fish exposed to 0.2 mg/l in the water. Lu and Metcalf (1975) studied the fate of radiolabeled pentachlorophenol in a model aquatic ecosystem with a six element food chain. Pentachlorophenol was reported to be ecologically magnified (bioconcentrated) in the mosquito fish, Gambusia affinis.

Several investigations have documented the distribution of pentachlorophenol in the aquatic environment. Rudling (1970) observed a 1000-fold concentration of the compound in the eel, Anguilla anguilla, living in lake water that had been contaminated with a 3 μg/l concentration of pentachlorophenol from pulp mill discharges. Zitko *et al*. (1974) carried out a survey of levels of pentachlorophenol in estuarine fauna in New Brunswick, Canada, and found low, but easily detectable amounts in most of the samples (Table 87-1).

Pierce and Victor (1978) studied the fate of pentachlorophenol in a freshwater lake near Hattiesburg, Mississippi, after accidental spills of wood-treating PCP-containing wastes in fuel oil. Pentachlorophenol was found to persist in the water and in fish for over six months following the

Table 87-1

Concentration of Pentachlorophenol in estuarine fauna (Zitko _et_ _al_. 1974).

Sample	Sample weight (g)	Pentachlorophenol (ng/g wet weight)
Cod	486.8	0.82
Winter flounder	157.8	1.77
	128.2	3.99
Sea raven	875.9	<0.5
Silver hake	214.0	1.75
Atlantic salmon	50.3	1.26
	8.5	0.54
White shark liver	-	10.83
Double-crested cormorant egg	46.2	0.36
Herring gull egg	96.1	0.51

spills. Fish were also observed to accumulate several of the degradation products of PCP, namely, pentachloroanisole and the 2,3,5,6- and 2,3,4,5-tetrachlorophenol isomers. The bioaccumulation of pentachloroanisole is to be expected, based upon its log octanol/water partition coefficient (log P = 5.66; calculated by the method of Tute 1971).

Pierce and Victor (1978) found that fish liver developed the highest concentration of pentachlorophenol followed by gill and muscle tissue. Zitko et al. (1974) and Holmberg et al. (1972) likewise observed higher levels of the compound in the liver compared to the muscle of marine fish and the yellow eel. Contrary to these observations, Statham et al. (1976) found the highest bioconcentration of radiolabeled pentachlorophenol in the rainbow trout (*Salmo gairdneri*) to occur in the gill. Kobayashi and Akitake (1975), however, reported that the highest concentration of pentachlorophenol was found in the gall bladder of fish.

Although a rapid uptake of pentachlorophenol has been observed in many organisms, depuration also appears to be significant. Kobayashi and Akitake (1975) reported that goldfish excreted 50 percent of absorbed pentachlorophenol within 10 hours after transfer to fresh running water. The concentration decreased to approximately 20 percent of initial levels after 20 hours. Holmberg et al. (1972) observed that pentachlorophenol in the muscle of the yellow eel, (*Anguilla anguilla*) decreased from 9.4 μg/g of tissue to 3.6 μg/g after 8 days in clean water.

87.4.7 Biotransformation and Biodegradation

The microbial degradation of chlorophenols under laboratory conditions has been discussed by several investigators (Alexander and Aleem 1961; Watanabe 1973; Nachtigall and Butler 1974; Gee and Peel 1974). In general, chlorophenols are more resistant to biological degradation than phenols. Highly chlorinated phenols, particularly those with halogens at the meta position on the ring, are the most resistant to degradation (Alexander and Aleem 1961).

The microbial degradation of pentachlorophenol, however, has been observed in several laboratory investigations in which the compound was used as the sole carbon source provided to microorganisms. Chu and Kirsch (1972) observed the oxidation of pentachlorophenol by bacteria obtained from a continuous flow enrichment culture. Watanabe (1973) reported on the ability of *Pseudomonas* sp., isolated from PCP-saturated soil cultures, to grow in the presence of 40 ppm pentachlorophenol as the sole carbon source. The data presented by Kirsch and Etzel (1973) also indicates that pentachlorophenol is amenable to microbial degradation under laboratory conditions. These investigators found that the rate of decomposition is dependent on a number of variables, particularly the bacterial concentration and the amount of aeration.

Microbial decomposition of pentachlorophenol in soil and axenic cultures has been studied by several investigators (Alexander and Aleem 1961; Kuwatsuka 1972; and Kirsch and Etzel 1973) who have reported the presence of two decomposition products, a tri- and a tetrachlorophenol that were relatively stable to further decomposition. Pierce and Victor (1978), in one of the few studies to investigate the fate of pentachlorophenol in a natural aquatic environment, documented the presence of pentachloroanisole and the 2,3,5,6- and 2,3,4,5-tetrachlorophenol isomers as major degradation products. Cserjesi and Johnson (1972) observed the methylation of pentachlorophenol to pentachloroanisole by the fungi, Trichoderma virgatum. They noted, however, that the formation of pentachloroanisole did not account for the total reduction in the concentration of pentachlorophenol in the growth medium and concluded that methylation is either the first step in the metabolism of this compound or a reaction parallel to degradation.

Pentachlorophenol has been shown to be detoxified by fish and other aquatic organisms in several laboratory investigations. Akitake and Kobayashi (1975) found that the goldfish, Carassius auratus, transformed pentachlorophenol to a pentachlorophenyl sulfate, which was identical to that found in the littleneck clam (Kobayashi et al. 1970). Lu and Metcalf (1975) also noted that conjugation at the phenolic hydroxy group was the most important detoxification mechanism among the organisms they studied in their model aquatic ecosystem. Studies in man indicate that the primary route for removal of pentachlorophenol in mammals, including man, is urinary excretion of a conjugate form (Jacobson and Yelner 1971; Braun and Sauerhoff 1976).

87.5 Data Summary

Table 87-2 summarizes the aquatic fate data for this pollutant. Photolysis and degradation appear to be highly effective fate processes for pentachlorophenol. This pollutant does not appear to be persistent in the aqueous medium itself but it is definitely sorbed by the organic matter of soils and sediments in a freshwater ecosystem. Moreover, it has been shown to be bioaccumulated by numerous aquatic organisms. The persistence of degradation products may be important and one of them, pentachloroanisole, probably has a greater tendency for bioaccumulation than the pollutant itself. Oxidation, hydrolysis, and volatilization are probably of very little environmental consequence.

Table 87-2

Summary of Aquatic Fate of Pentachlorophenol

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis[a]	Photolysis of pentachlorophenol is reported to occur under natural conditions and it is probably an important process near the water surface.	$3.4 \times 10^{-4} sec^{-1}$ [b]	4.75 hours[b] 1.5 days[c]	High
Oxidation	No specific information found; is thought not to be an important process.	-	-	Low
Hydrolysis	No specific information found; is thought not to be an important process.	-	-	Low
Volatilization	Probably does not affect the aquatic fate of this pollutant.	-	-	Low
Sorption	Definitely sorbed by the leaf litter and other organic matter in the soil and sediments of the watershed of a fresh-water lake.	-	-	High
Bioaccumulation	Has been shown to bioaccumulate in numerous aquatic organisms.	-	-	High
Biotransformation/ Biodegradation[a]	In a well-documented study of a fresh-water lake, two accidental spills were metabolized to pentachloroanisole and a mixture of chlorinated phenols.	-	-	High

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a. Both photolysis and biodegradation appear to be important fate processes.

b. The rate was determined at pH 7 with a light intensity of 0.04 watts/cm^2 between 290 and 330 nm. The half-life was calculated for a depth of 300 cm on a midsummer day at the latitude of Cleveland, Ohio (Hiatt _et al_. 1960).

c. The half-life was estimated from the data of Wong and Crosby (1978) for photolytic destruction by sunlight in an aqueous solution at Davis, California.

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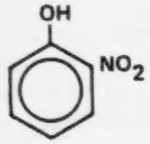
88. 2-NITROPHENOL

88.1 Statement of Probable Fate

Based on the information gathered for 2-nitrophenol, 4-nitrophenol, and 2,4-dinitrophenol, 2-nitrophenol will probably undergo slow photooxidation in an aerated aquatic environment. There is a possibility for photoreduction of the nitro group if the 2-nitrophenol becomes absorbed by organic particulates. 2-Nitrophenol should be strongly sorbed by clay minerals and may even undergo hydrolysis within the clay structure. Volatilization and bioaccumulation appear to be unlikely processes, and although biotransformation of 2-nitrophenol has been demonstrated, the nitrophenols are very persistent in aqueous mixed cultures and will inhibit microbial growth in natural aquatic systems into which they are introduced.

88.2 Identification

2-Nitrophenol has been detected in river water and in industrial effluents (Shackelford and Keith 1976). The chemical structure of 2-nitrophenol is shown below.



2-Nitrophenol

CAS NO. 88-75-5
TSL NO. SM 21000

Alternate Names

o-Nitrophenol
2-Hydroxynitrobenzene

88.3 Physical Properties

The general physical properties of 2-nitrophenol are as follows.

Molecular weight (Weast 1977)	139.11
Melting point (Weast 1977)	45.3°
Boiling point at 760 torr (Weast 1977)	216°C

Vapor pressure at 49.3°C (Weast 1977)	1.0 torr
Solubility in water at 20°C (Verschueren 1977)	2,100 mg/l
Log octanol/water partition coefficient (Leo *et al*. 1971)	1.76
pK_a (Pearce and Simkins 1968)	7.21

88.4 Summary of Fate Data

88.4.1 Photolysis

2-Nitrophenol is a somewhat acidic substance, $pK_a = 7.21$ (Pearce and Simkins 1968), and will exist to an appreciable extent as an anion in environmental surface waters. The ultraviolet absorption spectrum of 2-nitrophenol in methanol exhibits a maximum at about 345 nm which extends out beyond 400 nm (Sadtler Standard Spectra 1975). The intensity of absorption increases markedly near 410 nm in basic solutions.

Nakagawa and Crosby (1974) report that 4-nitrophenol was degraded in aqueous solutions within a period of 1-2 months when it was exposed to sunlight at a concentration of 200 mg/l. The principal products were hydroquinone and 4-nitrocatechol. A dark, acidic intractable polymer was also produced. Although no specific information was found in the reviewed literature demonstrating that 2-nitrophenol would also be photochemically hydroxylated in an analogous manner, the following mechanistic considerations for this photochemical reaction indicate that, under similar conditions, 2-nitrophenol would give rise to catechol and 2-nitrohydroquinone.

Nakagawa and Crosby (1974) proposed that the observed reaction products arising from 4-nitrophenol were the result of photonucleophilic displacement reactions involving water or hydroxide ion. This type of reaction mechanism could be rationalized for the formation of hydroquinone, but it is probably not valid in the case of 4-nitrocatechol since it is difficult to envision the development of a center of electron deficiency on the unsubstituted carbon atom adjacent to the phenolic group. Suarez *et al*. (1970) and Günther *et al*. (1971) have demonstrated that hydroxyl radicals preferentially attack 4-nitrophenol in water at the C-2 and C-4 positions, and that the latter intermediate results in the displacement of the nitro group by a hydroxy group. Although attack by hydroxyl radical can more easily explain the observed products, it is uncertain whether the concentration of hydroxyl radicals in the experiment of Nakagawa and Crosby

(1974) would have been sufficient to be responsible for the formation of hydroquinone and 4-nitrocatechol.

It has been reported that the ultraviolet irradiation of individual nitrophenolic compounds at 254 nm was without effect (Mitchell 1961). This experiment, however, was conducted by irradiating the nitro substituted phenol for 30 minutes after it had been applied in solution to a sheet of chromatographic paper which was then dried. The experiment was one of very short duration and the conditions were anhydrous or hypohydrous. For these reasons it is probably not valid to draw any conclusions from this experiment with respect to either the aquatic or terrestrial environment.

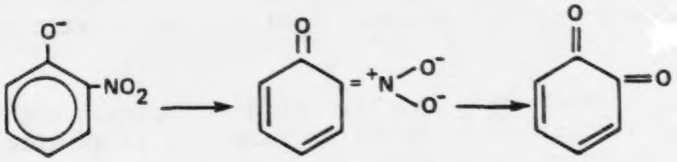
A further photochemical reaction of 2-nitrophenol that must be considered is photoreduction of the nitro group. As an example, Nakagawa and Crosby (1974) found that the nitro group of nitrofen, a nitroaromatic pesticide, underwent photochemical reduction to amino and azo groups in an aqueous solution that contained 10% methanol. Aromatic nitro groups are, in general, reduced photochemically in the presence of suitable hydrogen donors (Morrison 1969). Since the log octanol/water partition coefficient of 2-nitrophenol indicates a slight potential for absorption by aquatic organic matter, this organic material could serve as a reducing agent in the photoreduction of 2-nitrophenol to 2-aminophenol and 2,2'-dihydroxyazobenzene. No specific information was found pertaining to photoreduction of 2-nitrophenol in the reviewed literature.

88.4.2 Oxidation

Suarez et al. (1970) and Günther et al. (1971) have demonstrated that hydroxyl radicals attack 2-nitrophenol at the C-2 and C-4 positions resulting in the formation of a complex mixture that follows from the generation of 1,2-benzosemiquinone. No information was found, however, from which an environmentally relevant rate could be estimated for this reaction.

88.4.3 Hydrolysis

The covalent bond of a substituent attached to an aromatic ring is usually resistant to hydrolysis because of the high negative charge-density of the aromatic nucleus. Nonetheless, there is a possibility, albeit not specifically substantiated in the reviewed literature, that nitrophenols could undergo hydrolysis while sorbed by clay minerals. Specifically, 4-nitrophenol is not only adsorbed by montmorillonite but also becomes intercalated within the clay structure (Saltzman and Yariv 1975), and there is no apparent reason to believe that 2-nitrophenol would behave differently. The water molecules within the clay structure can be highly acidic, and the phenolic group of the intercalated 2-nitrophenol would become more acidic than when the molecule is in aqueous solution due to coordination of the phenolic oxygen atom with the metal cations of the clay. This acidic environment could conceivably lead to the hydrolysis of the 2-nitrophenol anion in a manner similar to the hydrolysis of _aci_-nitroparaffins (Johnson and Degering 1943). The resulting compound would be 1,2-benzoquinone.



88.4.4 Volatilization

Compounds which exert high vapor pressures are generally considered volatile and thus have a greater tendency to enter the atmosphere from an aqueous system than do those compounds having a low vapor pressure. The vapor pressure of 2-nitrophenol at somewhat elevated temperatures (49°C) is only 1.0 torr. The vapor pressure of 2-nitrophenol under ambient conditions would be even less and, as a result, volatilization is an unlikely transport process. In addition, the high solubility of 2-nitrophenol in water (2,100 mg/l at 20°C) favors a partitioning tendency toward water rather than air. A further factor which must be taken into consideration is the ionization of the molecule in an aqueous medium. The value of the pK_a (7.21; Pearce and Simkins 1968) indicates that about one-half of the molecules of this pollutant will be present as non-volatile anions in circumneutral water.

88.4.5 Sorption

The moderate value of the octanol/water partition coefficient indicated by log P = 1.76 (Leo _et al_. 1971) suggests only limited potential for sorption of 2-nitrophenol by organic particulates. In contrast, the stability of the clay complexes of 4-nitrophenol, an isomer of 2-nitrophenol, appears to be considerable, e.g., 4-nitrophenol cannot be desorbed from montmorillonite even when the clay complex is heated under reduced pressure (Saltzman and Yariv 1975). It is uncertain whether 2-nitrophenol will behave similarly since there is a sizable amount of intramolecular interaction between the nitro group and the adjacent hydroxy group (Morrison and Boyd 1973) which could interfere with the formation of such unusually stable organic-inorganic complexes. From the data of Chang and Anderson (1968), however, 2-nitrophenol appears to be an effective flocculating agent for clays and soils in aqueous suspension. These latter observations imply that 2-nitrophenol does form stable organic-inorganic aggregates in an aqueous medium.

88.4.6 Bioaccumulation

Based upon the observed relationship of the octanol/water partition coefficient and a compound's tendency to bioaccumulate in aquatic systems (Neely et al. 1974), nitrophenols in general are not expected to bioaccumulate in aquatic organisms. Further support for this contention is given by the study of Lu and Metcalf (1975) on the biomagnification of nitroaromatic compounds. Nitrobenzene itself was not found to be biomagnified, and the fish in the model aquatic ecosystem excreted the nitrobenzene primarily in the form of 4-nitrophenol.

88.4.7 Biotransformation and Biodegradation

All nitrophenols inhibit the microbial growth of natural aquatic systems because they uncouple the metabolic process of oxidative phosphorylation (Howard et al. 1976; Makhinya 1966). Most of the studies of microbial degradation of nitrophenols have concentrated on the isolation of pure cultures which can utilize these pollutants as sources of energy, carbon, or nitrogen (Howard et al. 1976). It is questionable whether these studies can be extrapolated to the environment of ambient surface waters since the concentration of the test chemical employed for enrichment of an organism and for obtaining a reasonable amount of cell growth is far above the concentrations generally found in nature.

There are only a few published studies regarding the breakdown of nitrophenolic compounds by natural communities of microorganisms (Howard et al. 1976). Brebion et al. (1967) examined the ability of the microorganisms taken from soil, water, and mud to degrade 4-nitrophenol. The cells were cultivated on a mineral nutrient solution in which nitrophenols were added as the sole source of carbon. The experimental findings revealed no significant removal of the compounds under these conditions. The fate of 2-, 3-, and 4-nitrophenol in the presence of natural communities of soil organisms has been studied also by Alexander and Lustigman (1966). A small amount of soil was suspended in water and the concentration of the nitrophenol was assayed by ultraviolet absorbance. The 2-nitrophenol was the most resistant to degradation and persisted unchanged for more than 64 days. The 3-nitrophenol and the 4-nitrophenol remained unchanged for 4 days and 16 days, respectively, before being gradually biodegraded. The three biotransformation processes that have been observed for 2-nitrophenol under optimal conditions of pure culture are reduction of the nitro group (McCormick et al. 1976), hydroxylation of the aromatic ring (Raymond and Alexander 1971), and displacement of the nitro group by a hydroxy group (Raymond and Alexander 1971; Siddaramappa et al. 1973; Munnecke and Hsieh 1974).

88.5 Data Summary

Table 88-1 summarizes the aquatic fate data for 2-nitrophenol. Nitrophenols interfere with biological oxidative phosphorylation and thereby can greatly inhibit the microbial growth of aquatic systems into which they are introduced. 2-Nitrophenol will probably undergo slow photolytic destruction in ambient surface waters. Volatilization is not thought to be an important transport process but 2-nitrophenol should be strongly sorbed by clay minerals. There is a possibility that 2-nitrophenol could undergo hydrolysis within the clay structure. Although the biotransformation of 2-nitrophenol has been demonstrated, it appears to be very persistent in aqueous mixed cultures.

Table 88-1

Summary of Aquatic Fate of 2-Nitrophenol

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis[a]	Based on information found for 4-nitrophenol, slow photolysis may be the main degradative pathway.	–	–	Low
Oxidation	Oxidation by hydroxyl radical has been demonstrated.	–	–	Low
Hydrolysis	There is a slight possibility of hydrolysis if 2-nitrophenol becomes sorbed by clay minerals.	–	–	Low
Volatilization	Volatilization is probably not important.	–	–	Medium
Sorption	Adsorption by clay minerals has been demonstrated.	–	–	Medium
Bioaccumulation	Probably not important.	–	–	Low
Biotransformation/ Biodegradation	2-Nitrophenol is persistent in mixed aqueous cultures and also inhibits the aerobic microbial growth of aquatic systems through its action as an oxidative phosphorylation uncoupler.	–	–	High

---

a. The predominant environmental process which is thought to determine the fate of the compound.

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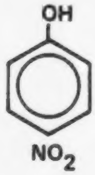
89. 4-NITROPHENOL

89.1 Statement of Probable Fate

4-Nitrophenol will probably undergo slow photoxidation in an aerated aquatic environment. There is, however, a possibility for photoreduction of the nitro group if the 4-nitrophenol becomes absorbed by organic particulates. 4-Nitrophenol will be strongly sorbed by clay minerals and may even undergo hydrolysis within the clay structure. Volatilization and bioaccumulation appear to be unlikely processes, and although biotransformation of 4-nitrophenol has been demonstrated, the nitrophenols are very persistent in aqueous mixed cultures and will inhibit microbial growth in natural aquatic systems into which they are introduced.

89.2 Identification

4-Nitrophenol has been detected in industrial effluents (Shackelford and Keith 1976). The chemical structure of 4-nitrophenol is shown below.



4-Nitrophenol

Alternate Names

p-Nitrophenol
4-Hydroxynitrobenzene

CAS NO. 100-07-7
TSL NO. SM 22750

89.3 Physical Properties

The general physical properties of 4-nitrophenol are as follows.

Molecular weight (Weast 1977)	139.11
Melting point (Weast 1977)	114.9°C
Boiling point at 760 torr (Weast 1977)	279°C
Vapor pressure at 146°C (Verschueren 1977)	2.2 torr

Solubility in water at 25°C (Verschueren 1977)	16,000 mg/l
Log octanol/water partition coefficient (Leo *et al*. 1971)	1.91
pK_a (Pearce and Simkins 1968)	7.15

89.4 Summary of Fate Data

89.4.1 Photolysis

4-Nitrophenol is a somewhat acidic substance, $pK_a = 7.15$ (Pearce and Simkins 1968), and will exist to an appreciable extent as an anion in environmental surface waters. The ultraviolet absorption spectrum of 4-nitrophenol in methanol exhibits a maximum at about 310 nm which extends out to 400 nm (Verzilina and Belotsvetov 1969). The intensity of absorption near 400 nm is enhanced in basic solutions.

Nakagawa and Crosby (1974) report that 4-nitrophenol was degraded in aqueous solution within a period of 1-2 months when it was exposed to sunlight at a concentration of 200 mg/l. The principal products were hydroquinone and 4-nitrocatechol. A dark, acidic intractable polymer was also produced. Nakagawa and Crosby (1974) propose that the observed reaction products arose via photonucleophilic displacement reactions involving water or hydroxide ion. This type of reaction mechanism might be easily rationalized for the formation of hydroquinone, but it is probably not valid in the case of 4-nitrocatechol since it is difficult to envision the development of a center of electron deficiency on the unsubstituted carbon atom adjacent to the phenolic group.

Suarez *et al*. (1970) and Günther *et al*. (1971) have demonstrated that hydroxyl radicals preferentially attack 4-nitrophenol in water at the C-2 and C-4 positions, and that the latter intermediate results in the displacement of the nitro group by a hydroxy group. Although attack by hydroxyl radical can more easily explain the observed products, it is uncertain whether the concentration of hydroxyl radicals in the experiment of Nakagawa and Crosby (1974) would have been sufficient to be responsible for the formation of hydroquinone and 4-nitrocatechol.

It has been reported that the ultraviolet irradiation of individual nitrophenols at 254 nm was without effect (Mitchell 1961). This experient, however, was conducted by irradiating the nitro substituted phenol for 30 minutes after it had been applied in solution to a sheet of chromatographic paper which was then dried. The experiment was one of very short duration and the conditions were anhydrous or hypohydrous. It is, there-

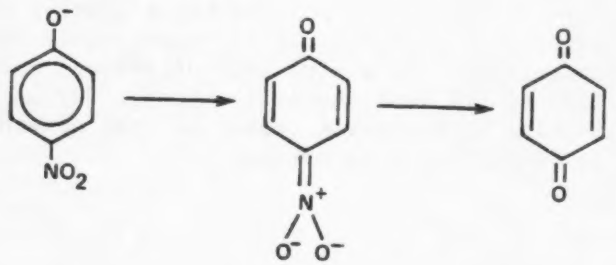
A further photochemical reaction of 4-nitrophenol that must be considered is photoreduction of the nitro group. As an example, Nakagawa and Crosby (1974) found that the nitro group of nitrofen, a nitroaromatic pesticide, underwent photochemical reduction to amino and azo groups in an aqueous solution that contained 10% methanol. Since the log octanol/water partition coefficient of 4-nitrophenol indicates a slight potential for absorption by suspended organic matter, this organic material could serve as a reducing agent in the photoreduction of 4-nitrophenol to 4-aminophenol and 4,4'-dihydroxyazobenzene. No specific information was found pertaining to photoreduction of 4-nitrophenol in the reviewed literature.

89.4.2 Oxidation

Suarez *et al*. (1970) and Günther *et al*. (1971) have demonstrated that hydroxyl radicals attack 4-nitrophenol at the C-2 and C-4 positions resulting in the formation of a complex mixture, the principal products of which are hydroquinone and 1,4-benzoquinone. No information was found, however, from which an environmentally relevant rate could be estimated for this reaction.

89.4.3 Hydrolysis

The covalent bond of a substituent attached to an aromatic ring is usually resistant to hydrolysis because of the high negative charge-density of the aromatic nucleus. Nonetheless, there is a possibility, albeit not specifically substantiated in the reviewed literature, that nitrophenols could undergo hydrolysis while sorbed by clay minerals. 4-Nitrophenol is not only adsorbed by montmorillonite but also becomes intercalated within the clay structure (Saltzman and Yariv 1975). The water molecules within the clay structure can be highly acidic, and the phenolic group of the intercalated 4-nitrophenol itself is more acidic than when the molecule is in aqueous solution due to coordination of the phenolic oxygen atom with the metal cations of the clay. This acidic environment could conceivably lead to the hydrolysis of the 4-nitrophenol anion in a manner similar to the hydrolysis of *aci*-nitroparaffins (Johnson and Degering 1943). The resulting compound would be 1,4-benzoquinone.



89.4.4 Volatilization

The vapor pressure of 4-nitrophenol at elevated temperatures (146°C) is only 2.2 torr. The vapor pressure of 4-nitrophenol under ambient conditions would be even less and, as a result, volatilization is a highly unlikely transport process. In addition, the high solubility of 4-nitrophenol in water (16,000 mg/l at 25°C) favors a partitioning tendency toward water rather than air. 4-Nitrophenol, in fact, does not even volatilize from boiling water due to intermolecular hydrogen bonding (Morrison and Boyd 1973).

89.4.5 Sorption

The moderate value of the octanol/water partition coefficient indicated by log P = 1.91 (Leo et al. 1971) suggests only slight potential for sorption by organic particulates. The stability of the clay complexes of 4-nitrophenol, however, appears to be considerable. Intercalation of 4-nitrophenol within the structure of montmorillonite involves both ionic attraction and orbital overlap. 4-Nitrophenol cannot be desorbed from montmorillonite even when the clay complex is under reduced pressure (Saltzman and Yariv 1975).

89.4.6 Bioaccumulation

Based upon the observed relationship of the octanol/water partition coefficient and a compound's tendency to bioaccumulate in aquatic systems (Neely et al. 1974), nitrophenols in general are not expected to bioaccumulate in aquatic organisms. Further support for this contention is given by the study of Lu and Metcalf (1975) on the biomagnification of nitroaromatic compounds. Nitrobenzene itself was not found to be biomagnified, and the fish in the model aquatic ecosystem excreted the nitrobenzene primarily in the form of 4-nitrophenol.

89.4.7. Biotransformation and Biodegradation

All nitrophenols inhibit the microbial growth of natural aquatic systems because they uncouple the metabolic process of oxidative phosphorylation (Howard et al. 1976; Makhinya 1966). Most of the studies of microbial degradation of nitrophenols have concentrated on the isolation of pure cultures which can utilize these pollutants as sources of energy, carbon, or nitrogen (Howard et al. 1976). It is questionable whether these studies can be extrapolated to the environment of ambient surface waters since the concentration of the test chemical employed for enrichment of an organism and for obtaining a reasonable amount of cell growth is far above the concentrations generally found in nature.

There are only a few published studies regarding the breakdown of nitrophenolic compounds by natural communities of microorganisms (Howard et al. 1976). Brebion et al. (1967) examined the ability of the microorganisms taken from soil, water, and mud to degrade 4-nitrophenol. The cells were cultivated on a mineral nutrient solution in which nitrophenols were added as the sole source of carbon. The experimental findings revealed no significant removal of the compounds under these conditions. The fate of 2-, 3-, and 4-nitrophenol in the presence of natural communities of soil organisms has been studied also by Alexander and Lustigman (1966). A small amount of soil was suspended in water and the concentration of the nitrophenol was assayed by ultraviolet absorbance. The 2-nitrophenol was the most resistant to degradation and persisted unchanged for more than 64 days. The 3-nitrophenol and 4-nitrophenol remained unchanged for 4 days and 16 days, respectively, before being gradually biodegraded. The three biotransformation processes that have been observed for nitrophenols are reduction of the nitro group (McCormick et al. 1976), hydroxylation of the aromatic ring (Raymond and Alexander 1971), and displacement of the nitro group by a hydroxy group (Raymond and Alexander 1971; Siddaramappa et al. 1973; Munnecke and Hsieh 1974).

89.5 Data Summary

Table 89-1 summarizes the aquatic fate data for 4-nitrophenol. Nitrophenols interfere with biological oxidative phosphorylation and thereby can greatly inhibit the microbial growth of aquatic systems into which they are introduced. 4-Nitrophenol will probably undergo slow photolytic destruction in ambient surface waters. Volatilization is not thought to be an important transport process but 4-nitrophenol should be strongly sorbed by clay minerals. There is a possibility that 4-nitrophenol could undergo hydrolysis within the clay structure. Although the biotransformation of 4-nitrophenol has been demonstrated, it appears to be very persistent in aqueous mixed cultures.

Table 89-1

Summary of Aquatic Fate of 4-Nitrophenol

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis[a]	Slow photolysis may be the main degradative pathway.	-	-	Medium
Oxidation	Oxidation by hydroxyl radical has been demonstrated.	-	-	Low
Hydrolysis	There is a slight possibility of hydrolysis if 4-nitrophenol becomes sorbed by clay minerals.	-	-	Low
Volatilization	Volatilization is not important.	-	-	High
Sorption	Adsorption by clay minerals has been demonstrated.	-	-	High
Bioaccumulation	Probably not important	-	-	Low
Biotransformation/ Biodegradation	4-Nitrophenol is persistent in mixed aqueous cultures and also inhibits the aerobic microbial growth of aquatic systems through its action as an oxidative phosphorylation uncoupler.	-	-	High

---

a. The predominant environmental process which is thought to determine the fate of the compound.

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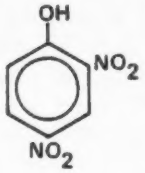
90. 2,4-DINITROPHENOL

90.1 Statement of Probable Fate

Based on the information gathered for 2-nitrophenol, 4-nitrophenol, and this pollutant, 2,4-dinitrophenol will probably undergo slow photooxidation in an aerated aquatic environment. There is a possibility for photoreduction of the nitro group if the 2,4-dinitrophenol becomes absorbed by organic particulates. 2,4-Dinitrophenol should be strongly sorbed by clay minerals, and may even undergo hydrolysis within the clay structure. Volatilization and bioaccumulation appear to be unlikely processes, and although biotransformation of 2,4-dinitrophenol has been demonstrated, the nitrophenols are very persistent in aqueous mixed cultures and will inhibit aerobic microbial growth in any natural aquatic systems in which they are present.

90.2 Identification

The chemical structure of 2,4-dinitrophenol is shown below.



2,4-Dinitrophenol

Alternate Names

Aldifen
2,4-DNP

CAS NO. 51-28-5
TSL NO. SL 28000

90.3 Physical Properties

The general physical properties of 2,4-dinitrophenol are as follows.

Molecular weight (Weast 1977)	184.11
Melting point (Verschueren 1977)	114°C
Boiling point	No data found
Vapor pressure	No data found

Solubility in water at 18°C (Verschueren 1977)	5,600 mg/l
Log octanol/water partition coefficient (Leo *et al.* 1971)	1.53
pK_a (Pearce and Simkins 1968)	4.09

90.4 Summary of Fate Data

90.4.1 Photolysis

2,4-Dinitrophenol is a moderately acidic substance, $pK_a=4.09$ (Pearce and Simkins 1968), and will exist substantially as an anion in environmental surface waters. The ultraviolet absorption spectrum of 2,4-dinitrophenol in methanol exhibits a maximum at about 290 nm which extends out beyond 400 nm (Verzilina and Belotsvetov 1969).

Nakagawa and Crosby (1974) report that 4-nitrophenol was degraded in aqueous solutions within a period of 1-2 months when it was exposed to sunlight at a concentration of 200 mg/l. The principal products were hydroquinone and 4-nitrocatechol. A dark, acidic intractable polymer was also produced. Although no specific information was found in the reviewed literature demonstrating that 2,4-dinitrophenol would also be photochemically hydroxylated in an analogous manner, the following mechanistic considerations for this photochemical reaction indicate that, under similar conditions, 2,4-dinitrophenol should be degraded to a mixture of compounds which would include 4-nitrocatechol, 2-nitrohydroquinone, and 3,5-dinitrocatechol.

Nakagawa and Crosby (1974) proposed that the observed reaction products arising from 4-nitrophenol were the result of photonucleophilic displacement reactions involving water or hydroxide ion. This type of reaction mechanism could be rationalized for the formation of hydroquinone, but it is probably not valid in the case of 4-nitrocatechol since it is difficult to envision the development of a center of electron deficiency on the unsubstituted carbon atom adjacent to the phenolic group. Suarez *et al.* (1970) and Günther *et al.* (1971) have demonstrated that hydroxyl radicals preferentially attack 4-nitrophenol in water at the C-2 and C-4 positions, and that the latter intermediate results in the displacement of the nitro group by a hydroxy group. Even though attack by hydroxyl radical can more easily explain the observed products, it is uncertain whether the concentration of hydroxyl radicals in the experiment of Nakagawa and Crosby (1974) would have been sufficient to be responsible for the formation of hydroquinone and 4-nitrocatechol.

It has been reported that the ultraviolet irradiation of individual nitrophenols at 254 nm was without effect (Mitchell 1961). This experiment, however, was conducted by irradiating the nitrosubstituted phenol for 30 minutes after it had been applied in solution to a sheet of chromatographic paper which was then dried. The experiment was one of very short duration and the conditions were anhydrous or hypohydrous. For these reasons it is probably not valid to draw any conclusions from this experiment with respect to either the aquatic or terrestrial environment.

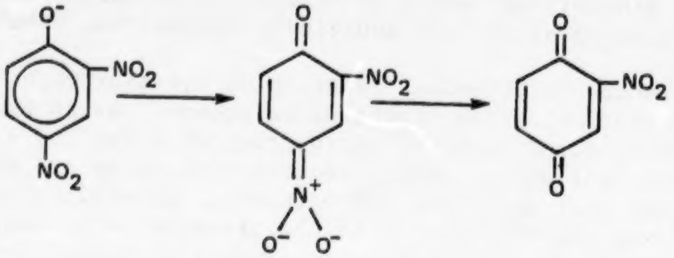
A further photochemical reaction of 2,4-dinitrophenol that must be considered is photoreduction of the nitro groups. As an example, Nakagawa and Crosby (1974) found that the nitro group of nitrofen, a nitroaromatic pesticide, underwent photochemical reduction to amino and azo groups in an aqueous solution that contained 10% methanol. Aromatic nitro groups are generally reduced photochemically in the presence of suitable hydrogen donors (Morrison 1969). The log octanol/water partition coefficient of 2,4-dinitrophenol indicates a slight potential for absorption by suspended aquatic organic matter. In this way the organic material could serve as a reducing agent in the photoreduction. Massini and Voorn (1967) report that the reduction of 2,4-dinitrophenol by ascorbic acid is sensitized by the presence of chlorophyll and is enhanced further by ferrous ion. The products of this reduction were not indicated but it is quite likely that a complex mixture of nitrogen compounds was produced.

90.4.2 Oxidation

Suarez et al. (1970) and Günther et al. (1971) have demonstrated that hydroxyl radicals attack both 2-nitrophenol and 4-nitrophenol at the C-2 and C-4 positions resulting in the formation of a complex mixture that follows from the generation of isomeric benzosemiquinones. No information was found, however, from which an environmentally relevant rate could be estimated for this reaction. It can be inferred that 2,4-dinitrophenol could be oxidized in an analogous fashion.

90.4.3 Hydrolysis

The covalent bond of a substituent attached to an aromatic ring is usually resistant to hydrolysis because of the high negative charge-density of the aromatic nucleus. Nonetheless, there is a possibility, albeit not specifically substantiated in the reviewed literature, that nitrophenols could undergo hydrolysis while sorbed by clay minerals. Specifically, 4-nitrophenol is not only adsorbed by montmorillonite but also becomes intercalated within the clay structure (Saltzman and Yariv 1975) and there is no apparent reason to believe that 2,4-dinitrophenol would be less likely to be similarly sorbed. The water molecules within the clay structure can be highly acidic, and the phenolic group of the intercalated 2,4-dinitrophenol would become more acidic than when the molecule is in aqueous solution due to coordination of the phenolic oxygen atom with the metal cations of the clay. This acidic environment could conceivably lead to hydrolysis of the 2,4-dinitrophenol anion in a manner similar to the hydrolysis of aci-nitroparaffins (Johnson and Degering 1943).



90.4.4 Volatilization

The vapor pressure of 4-nitrophenol at elevated temperatures (146°C) is only 2.2 torr. As a more highly substituted nitrophenol, the vapor pressure of 2,4-dinitrophenol under ambient conditions would be expected to be less, and as a result, volatilization is a highly unlikely transport process. In addition, the high solubility of 2,4-dinitrophenol in water (5,600 mg/l at 18°C) and its presence in solution primarily as an anion strongly favor a partitioning tendency toward water rather than air. It is reported that 4-nitrophenol does not even volatilize from boiling water (Morrison and Boyd 1973) and 2,4-dinitrophenol would be expected to behave similarly.

90.4.5 Sorption

The moderate value of the octanol/water partition coefficient indicated by log P = 1.53 (Leo et al. 1971) suggests only limited potential for sorption of 2,4-dinitrophenol by organic particulates. The stability of the clay complexes of 2-nitrophenol and 4-nitrophenol appears to be considerable (Saltzman and Yariv 1975; Chang and Anderson 1968), however, and there is no reason to believe that 2,4-dinitrophenol will not behave similarly.

90.4.6 Bioaccumulation

Based upon the observed relationship of the octanol/water partition coefficient and a compound's tendency to bioaccumulate in aquatic systems (Neely et al. 1974), nitrophenols in general are not expected to bioaccumulate in aquatic organisms. Further support for this contention is given by the study of Lu and Metcalf (1975) on the biomagnification of nitroaromatic compounds. Nitrobenzene itself was not found to be biomagnified and the fish in the model aquatic ecosystem excreted the nitrobenzene primarily in the form of 4-nitrophenol.

90.4.7 Biotransformation and Biodegradation

All nitrophenols inhibit the microbial growth of natural aquatic systems because they uncouple the metabolic process of oxidative phosphorylation (Howard et al. 1976; Makhinya 1966). Most of the studies of microbial degradation of nitrophenols have concentrated on the isolation of pure cultures which can utilize these pollutants as sources of energy, carbon, or nitrogen (Howard et al. 1976). It is questionable whether these studies can be extrapolated to the environment of ambient surface waters since the concentration of the test chemical employed for enrichment of an organism and for obtaining a reasonable amount of cell growth is far above the concentrations generally found in nature.

There are only a few published studies regarding the breakdown of nitrophenolic compounds by natural communities of microorganisms (Howard et al. 1976). Brebion et al. (1967) examined the ability of the microorganisms taken from soil, water, and mud to degrade 4-nitrophenol. The cells were cultivated on a mineral nutrient solution in which nitrophenols were added as the sole source of carbon. The experimental findings revealed no significant removal of the compounds under these conditions. The fate of 2-, 3-, and 4-nitrophenol in the presence of natural communities of soil organisms has been studied also by Alexander and Lustigman (1966). A small amount of soil was suspended in water and the degradation of the nitrophenol was assayed by ultraviolet absorbancy. The 2-nitrophenol was the most resistant to degradation and persisted unchanged for more than 64 days. The 3-nitrophenol and the 4-nitrophenol remained unchanged for 4 days and 16 days, respectively, before being gradually biodegraded. The three biotransformation processes that have been observed for 2,4-dinitrophenol under optimal conditions in pure culture are reduction of the nitro group (McCormick et al. 1976), hydroxylation of the aromatic ring (Raymond and Alexander 1971), and displacement of the nitro group by a hydroxy group (Raymond and Alexander 1971; Siddaramappa et al. 1973; Munnecke and Hsieh 1974).

90.5 Data Summary

Table 90-1 summarizes the aquatic fate data for 2,4-dinitrophenol. Nitrophenols interfere with biological oxidative phosphorylation and thereby can greatly inhibit the microbial growth of aquatic systems into which they are introduced. 2,4-Dinitrophenol will probably undergo slow photolytic destruction in ambient surface waters. Volatilization is not thought to be an important transport process but 2,4-dinitrophenol should be strongly sorbed by clay minerals. There is a possibility that 2,4-dinitrophenol could undergo hydrolysis within the clay structure. Although the biotransformation of 2,4-dinitrophenol has been demonstrated, this compound is probably very persistent in aqueous mixed cultures.

Table 90-1

Summary of Aquatic Fate of 2,4-Dinitrophenol

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis[a]	Based on information for 4-nitrophenol slow photolysis may be the main degradative pathway.	-	-	Low
Oxidation	Oxidation by aqueous hydroxyl radical has been demonstrated for 2-nitrophenol and 4-nitrophenol.	-	-	Low
Hydrolysis	There is a slight possibility of hydrolysis if 2,4-dinitrophenol becomes sorbed by clay minerals.	-	-	Low
Volatilization	Probably not important.	-	-	Low
Sorption	Adsorption by clay minerals should take place.	-	-	Low
Bioaccumulation	Probably not important.	-	-	Low
Biotransformation/ Biodegradation	2,4-Dinitrophenol can be degraded in isolated cultures but it should also inhibit the aerobic microbial growth of aquatic systems through its action as an oxidative phosphorylation uncoupler.	-	-	Medium

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a. The predominant environmental process which is thought to determine the fate of the compound.

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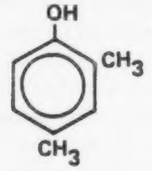
91. 2,4-DIMETHYLPHENOL (2,4-XYLENOL)

91.1 Statement of Probable Fate

There is a lack of data from which to assign a definitive environmental fate for 2,4-dimethylphenol. Based on the photolytic behavior of unsubstituted phenol and alkylbenzenes such as toluene, it can be inferred that 2,4-dimethylphenol will undergo photooxidation in the aquatic environment. It is not possible, however, to determine the relative importance of photooxidation in comparison to other possible fate processes. 2,4-Dimethylphenol has been reported to be readily degraded by activated sludge cultures but it appeared to be persistent in a simulated surface water environment.

91.2 Identification

2,4-Dimethylphenol has been detected in industrial effluents and in finished drinking water (Shackelford and Keith 1976).



2,4-Dimethylphenol

Alternate Names

2,4-Xylenol
1-Hydroxy-2,4-dimethylbenzene

CAS NO. 105-67-9
TSL NO. ZE 56000

91.3 Physical Properties

The general physical properties of 2,4-dimethylphenol are as follows.

Molecular weight (Weast 1977)	122.16
Melting point (Andon *et al*. 1960)	24.54°C
Boiling point at 760 torr (Andon *et al*. 1960)	210.93°C
Vapor pressure at 20°C (Andon *et al*. 1960)	0.0621 torr*

Solubility in water at 160°C (Erichsen and Dobbert 1955)	17,000 mg/l**
Log octanol/water partition coefficient (Calc. by method of Tute 1971)	2.50
pK_a (Herington and Kynaston 1957)	10.60

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* Vapor pressure of 2,4-dimethylphenol as a supercooled liquid.

**Solubilities of 3,5-dimethylphenol in water at 160°C and 20°C are 37,000 mg/l and 4,200 mg/l, respectively (Erichsen and Dobbert 1955).

91.4 Summary of Fate Data

91.4.1 Photolysis

2,4-Dimethylphenol is a very weak acid, $pK_a = 10.60$ (Herington and Kynaston 1957), and exists principally as its protonated, non-ionized form when it is in true solution in environmental surface waters. Coordination of the phenolic oxygen atom with dissolved or suspended di- and trivalent metal cations, however, can markedly increase the ionization of the phenolic proton. In the near ultraviolet spectral region the absorption maximum of undissociated 2,4-dimethylphenol occurs at 277 nm and extends to 300 nm while the anion of 2,4-dimethylphenol has an absorption maximum at 296 nm which extends beyond 320 nm (Herington and Kynaston 1957). It should be noted that complexes of phenolic compounds with metal cations, such as iron(III), absorb light strongly at about 600 nm (Ackermann and Hesse 1970). Any photolytic reactions of unsubstituted phenol that can occur in surface waters would, therefore, probably occur at an enhanced rate with this pollutant.

As an example, solid or liquid phenol has long been known to form reddish high molecular weight material when exposed to sunlight and air (Joschek and Miller 1966). A possible explanation for these observations could be the formation and photolysis of an oxygen-phenol charge-transfer complex. Joschek and Miller (1966) report that the steady irradiation of aqueous solutions of unsubstituted phenol at 254 nm in the presence of oxygen yields isolable amounts of 4,4'-dihydroxybiphenyl, 2,4'-dihydroxybiphenyl, 2,2'-dihydroxybiphenyl, hydroquinone, and catechol as well as many uncharacterized compounds. The latter two compounds predominate as products in the more dilute solutions. The intermediate that is postulated to explain this distribution of products is the phenoxyl radical.

Inasmuch as 2,4-dimethylphenol is a dimethyl substituted monocyclic aromatic compound, its photolytic behavior also should resemble that of toluene and m-xylene (1,3-dimethylbenzene). The primary photochemical process of toluene is generally regarded as a dissociation with formation of a benzyl radical (Porter and Norman 1954). Reaction of this benzyl radical with molecular oxygen is reported to be extremely fast ($k \sim 10^9$ $1.\ mole^{-1}\ sec^{-1}$) resulting in the production of benzyl hydroperoxide (Wei and Adelman 1969). Although benzyl hydroperoxide has considerable thermal stability, it can be photochemically transformed to benzyl alcohol and benzaldehyde. No information was found in the reviewed literature specifically pertaining to the photolysis of 2,4-dimethylphenol, but it can be inferred from the foregoing discussion that photolysis will be operative as a degradative pathway in well aerated surface waters.

91.4.2 Oxidation

Hydroxylation of aqueous phenol at the C-2 position in the presence of air and iron(III) or copper(II) ions has been reported but at temperatures and pressures far above what would be normally encountered in environmental surface waters (Makalets and Ivanova 1969). In addition, unsubstituted phenol has been oxidized by passing molecular oxygen into an aqueous solution at 25°C and pH 9.5-13 (Kirso et al. 1967). These observations, although not environmentally relevant in themselves, raise the possibility that 2,4-dimethylphenol could be non-photolytically oxidized in highly aerated waters which also contain iron and copper in solution or as part of the suspended particulates.

91.4.3 Hydrolysis

There are no data to suggest that hydrolysis of 2,4-dimethylphenol is an environmentally significant process. The covalent bond of a substituent attached to an aromatic ring is usually resistant to hydrolysis because of the high negative charge-density of the aromatic nucleus (Morrison and Boyd 1973).

91.4.4 Volatilization

The vapor pressure of supercooled liquid 2,4-dimethylphenol at 20°C is 0.0621 torr (Andon et al. 1960) and, based on the data of Erichsen and Dobbert (1955), the solubility at 20°C should be at least 1000 mg/l. Low vapor pressure and a moderately high solubility usually imply that there is little tendency for volatilization from water. Furthermore, it can be expected that aqueous 2,4-dimethylphenol also will be highly solvated which will increase its persistence in water at low levels of concentration.

91.4.5 Sorption

Unsubstituted phenol apparently has very little affinity for microcrystalline clays inasmuch as it can be almost completely desorbed from a thin layer of montmorillonite that has been exposed for one week to the atmosphere at 40% relative humidity (Saltzman and Yariv 1975). From the data of Chang and Anderson (1968), unsubstituted phenol also appears to be ineffective as a flocculant of clays and soils. This latter observation implies that unsubstituted phenol does not form stable organic-inorganic aggregates in an aqueous medium. 2,4-Dimethylphenol should behave similarly with regard to organic-inorganic interactions. 2,4-Dimethylphenol, however, has a log octanol/water partition coefficient of 2.50 (Tute 1971) and may, therefore, have some defininte tendency to become absorbed onto the organic detrius.

91.4.6 Bioaccumulation

Although the log octanol/water partition coefficient indicates that 2,4-dimethylphenol may have a tendency to be absorbed by aquatic biota, a review of the current literature revealed no information concerning the bioaccumulation of phenol by aquatic microorganisms or by aquatic invertebrates or vertebrates.

91.4.7 Biotransformation and Biodegradation

The microbial degradation of unsubstituted phenol has been observed in many laboratory studies in which phenol represented the primary carbon source provided for isolated and adapted microorganisms. Alexander and Lustigman (1966) observed that phenol was degraded rapidly by a mixed population of soil microorganisms. Their data suggested that the hydroxyl group, compared to other benzene ring substituents, facilitated microbial degradation. Some species of soil bacteria that have been demonstrated to be capable of utilizing toluene as a sole carbon source hydroxylate the aromatic ring to a mixture of methyl substituted phenolic compounds which are metabolized further to acetic acid and pyruvic acid (Claus and Walker 1964; Gibson *et al*. 1966). In addition, enrichment cultures of microorganisms obtained from garden soil, compost, river mud, and the sediment of a waste lagoon in a petroleum refinery were all shown to be capable of degrading 2,4-dimethylphenol (Tabak *et al*. 1964).

Biodegradation has been suggested as a mechanism for the degradation of phenolic wastes in natural waters (Streeter 1929; Happold and Key 1932; Mischonsniky 1934; Krombach and Barthel 1964; Polisois *et al*. 1975; Wuhrmann 1972), and recent studies have examined the importance of microorganisms in this process. Visser *et al*. (1977) conducted an *in situ* investigation of the phenol-degrading activity of bacteria in river water. Phenol (125 μg/l) was added to containers holding large quantities of river water. The containers were incubated in the river along with sterilized controls. The removal rate of phenol was 30 μg/l per hour from the natural samples compared to < 1 μg/l per hour from the sterilized controls.

2,4-Dimethylphenol has been reported to be almost completely degraded by the microorganisms of activated sludge cultures when the pollutant was used as the sole source of carbon (Pitter and Kucharova-Rosolova 1974). Kaplin et al. (1968), however, carried out a series of experiments in which they sought to duplicate the conditions for biodegradability that would occur in a river that was receiving phenolic waste effluents from a coking plant. Unsubstituted phenol decomposed rapidly, cresols exhibited a lag period of several days, but 2,4- and 2,3-dimethylphenol seemed to be very persistent.

91.5 Data Summary

Table 91-1 summarizes the aquatic fate data for phenol. Photooxidation appears to be a likely degradative pathway in the aquatic environment but the data regarding biodegradation are somewhat conflicting and inconclusive. Metal-catalyzed oxidation may be important in some localized situations. There may be some absorption by lypophilic materials but sorption by clay minerals appears unlikely. Volatilization and bioaccumulation are probably not important processes in this pollutant's fate.

Table 91-1

Summary of Aquatic Fate of 2,4-Dimethyl phenol

Environmental Process [a]	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Photooxidation may be an important degradative process in aerated clear surface waters.	-	-	Low
Oxidation	Metal-catalyzed oxidation may be relevant in some aerated surface waters.	-	-	Low
Hydrolysis	Not a relevant environmental process.	-	-	High
Volatilization	Not a significant process in the aquatic environment.	-	-	Low
Sorption	Probably not a significant process in the aquatic environment.	-	-	Low
Bioaccumulation	Probably not a significant process in the aquatic environment.	-	-	Low
Biotransformation/ Biodegradation	Available information is inconclusive with regard to degradation in natural surface waters.	-	-	Low

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

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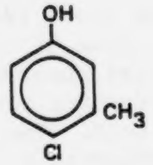
92. p-CHLORO-m-CRESOL

92.1 Statement of Probable Fate

The most probable aquatic fate of p-chloro-m-cresol is intramolecular photolysis. Although no specific data pertaining to the photolysis of p-chloro-m-cresol were found in the reviewed literature, this supposition is supported by the observed photolytic reductive dechlorination of 4-chlorophenol in 2-propanol and the well documented photochemistry of aromatic methyl substituents. No information was found in the reviewed literature in support of a role for oxidation and hydrolysis as fate pathways or for volatilization and sorption as transport processes. The importance of bioaccumulation cannot be ascertained from the available data, and it appears that although aerobic sewage plant treatment can effectively degrade p-chloro-m-cresol, it is uncertain whether biodegradation will be significant in ambient surface waters.

92.2 Identification

p-Chloro-m-cresol has been detected in both primary and secondary effluents (Shackelford and Keith 1976).



p-Chloro-m-cresol

CAS NO. 59-50-7
TSL NO. GO 71000

Alternate Names

4-Chloro-m-cresol
4-Chloro-3-methylphenol
2-Chloro-5-hydroxytoluene

92.3 Physical Properties

The general physical properties of p-chloro-m-cresol are as follows.

Molecular weight (Weast 1977)	142.59
Melting point (Weast 1977)	66°C
Boiling point at 760 torr (Weast 1977)	235°C
Vapor pressure	No data found

Solubility in water at 20°C (Windholz 1976)	3850 mg/l
Log octanol/water partition coefficient (Calc. by method of Tute 1971)	2.95
pK_a	No data found

92.4 Summary of Fate Data

92.4.1 Photolysis

No specific information pertaining to the photolysis of p-chloro-m-cresol was found in the reviewed literature. The ultraviolet absorption spectrum of the undissociated compound in methanol has a maximum at 281 nm that extends out to 300 nm while in basic solutions the maximum absorption peak of the anion shifts to 298 nm (Sadtler Standard Spectra 1975). These electromagnetic absorption characteristics are almost identical to those exhibited by the structurally similar compound, 4-chlorophenol (Drahonovsky and Vacek 1971), and it can, therefore, be expected by inference that the photolytic degradation of p-chloro-m-cresol will be similar in some ways to that of 4-chlorophenol.

Omura and Matsuura (1971) found that irradiation of 4-chlorophenol in aqueous alkali produced hydroquinone both at 254 nm and above 290 nm. When cyanide ion was present in the photolysis solutions, some of the substituent chlorine was replaced by cyano groups. This latter observation supports a reaction mechanism involving interaction of hydroxide ion in preference to water with the photolyzing carbon-chlorine bond. The photolysis of 4-chlorophenol to hydroquinone also has been reported by Grabowski (1961) at 313 nm indicating that it is probably the anionic form which undergoes carbon-chlorine fission.

The fact that the chlorine and methyl substituents occupy adjacent positions on the aromatic ring of p-chloro-m-cresol opens the possibility for photolytically induced interaction between these two groups. Pinhey and Rigby (1969) have reported that 4-chlorophenol readily undergoes photoreduction in 2-propanol to yield phenol. Analysis of the reaction mixture indicated that hydrogen atoms were being abstracted from the solvent, 2-propanol, by what can be assumed to be a phenoxyl radical and a chlorine atom. Insofar as the hydrogen atoms of aromatic methyl groups are easily abstracted, it is possible that intramolecular photolysis of p-chloro-m-cresol could produce a mixture of compounds from initial intermediates in which the methyl group had become chlorinated or had become oxidized to a benzyl hydroperoxide. Although no specific data pertaining to the aquatic photolysis of p-chloro-m-cresol were found in the reviewed literature, this supposition is supported by the observations of Pinhey and Rigby (1969) and the well documented photochemistry of aromatic methyl substituents (Porter and Norman 1954; Morrison 1969; Wei and Adelman 1969).

92.4.2 Oxidation

No information was found in the reviewed literature from which to assess the possibility of direct oxidation in the aquatic environment.

92.4.3 Hydrolysis

There are no data to suggest that hydrolysis of p-chloro-m-cresol is an environmentally significant process. The covalent bond of a substituent attached to an aromatic ring is usually resistant to hydrolysis because of the high negative charge-density of the aromatic nucleus (Morrison and Boyd 1973).

92.4.4 Volatilization

The fact that p-chloro-m-cresol has a boiling point of 235°C (Weast 1977) in addition to an aqueous solubility of 3850 mg/l at 20°C (Windholz 1976) indicates that volatilization from water at ambient environmental temperatures will not exert an overbearing consequence on the fate of this pollutant. Furthermore, aqueous p-chloro-m-cresol should be a weak acid that will be partially ionized and highly solvated, thus further increasing its persistence with respect to volatilization at low levels of concentration.

92.4.5 Sorption

Although the calculated value of the octanol/water partition coefficient indicated by log P = 2.95 suggests a definite potential for sorption of p-chloro-m-cresol by organic particulates, Zogorski and Faust (1976) have reported that some substituted phenolate anions are not easily sorbed from water by lipophilic materials. No information was found pertaining to the interaction of this pollutant with clay minerals.

92.4.6 Bioaccumulation

Calculation of the log octanol/water partition coefficient, using the method of Tute (1971), yields a value for log P of 2.95. This indicates that, except for the limits imposed by ionization and toxicity, this compound should normally exhibit a tendency to bioaccumulate. No information was found in the reviewed literature regarding the bioaccumulation of p-chloro-m-cresol.

92.4.7 Biotransformation and Biodegradation

The microbial breakdown of p-chloro-m-cresol has been examined under the simulated conditions of a wastewater treatment plant by Voets *et al*. (1976). Although quite susceptible to aerobic degradation in an organic supplemented medium, it was relatively persistent in an inorganic mineral medium, and it appeared to be completely resistant to anaerobic digestion.

Adapted mixed cultures, isolated by enrichment techniques from garden soil, compost, river mud, and the sediment of a petroleum refinery waste lagoon, were shown to be capable of partially degrading p-chloro-m-cresol (Tabak *et al*. 1964). It is questionable, however, whether these studies can be extrapolated to the environment of ambient surface waters since the concentration of the substrate chemical employed for enrichment of an organism and for obtaining a reasonable amount of cell growth is far above the concentrations generally found in nature.

92.5 Data Summary

Table 92-1 summarizes the aquatic fate data of p-chloro-m-cresol. The most probable fate is intramolecular photolysis. The operational likelihood of other fate processes does not appear to be tenable in ambient surface waters. Although aerobic sewage plant treatment can effectively degrade p-chloro-m-cresol, it is uncertain whether biodegradation will be significant in ambient surface waters.

Table 92-1

Summary of Aquatic Fate of p-Chloro-m-Cresol

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis[a]	Intramolecular photolysis is the most probable fate in ambient surface waters.	-	-	Low
Oxidation	Probably not significant.	-	-	Low
Hydrolysis	Not an environmentally relevant process.	-	-	Low
Volatilization	Probably not significant.	-	-	Low
Sorption	Insufficient data for definitive assessment; probably not important.	-	-	Low
Bioaccumulation	Probably not significant as an aquatic process.	-	-	Low
Biotransformation/ Biodegradation	Degraded during aerobic sewage plant treatment; but operational likelihood is uncertain in ambient surface waters.	-	-	Low

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a. The predominant environmental process which is thought to determine the fate of the compound.

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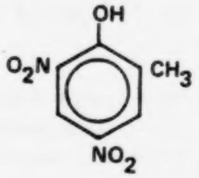
93. 4,6-DINITRO-o-CRESOL

93.1 Statement of Probable Fate

Based on the information gathered for nitrophenols and 4,6-dinitro-o-cresol itself, this pollutant will probably undergo slow photooxidation in an aerated aquatic environment. There is a possibility for photoreduction of the nitro group if the 4,6-dinitro-o-cresol becomes absorbed by organic particulates. 4,6-Dinitro-o-cresol should be strongly sorbed by clay minerals and may even undergo hydrolysis on the clay surface. Volatilization and bioaccumulation appear to be unlikely processes, and although biotransformation of 4,6-dinitro-o-cresol has been demonstrated, it is uncertain whether biodegradation will take place in ambient surface waters.

93.2 Identification

4,6-Dinitro-o-cresol has been identified in industrial effluents (Shackelford and Keith 1976). The chemical structure is shown below.



4,6-Dinitro-o-cresol

CAS NO. 534-52-1
TSL NO. GO 96250

Alternate Names

DNOC
2,4-Dinitro-6-methylphenol

93.3 Physical Properties

The physical properties of 4,6-dinitro-o-cresol are as follows.

Molecular weight (Verschueren 1977)	198.13
Melting point (Verschueren 1977)	85.8°C
Boiling point	No data found
Vapor pressure	No data found*

Solubility in water	No data found
Log octanol/water partition coefficient (Calc. by method of Tute 1971)	2.85
pK_a (Pearce and Simkins 1968)	4.35

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*The vapor pressure of pure 3,5-dinitro-o-cresol has been determined to be 5.2×10^{-5} torr at 20°C (Balson 1947).

93.4 Summary of Fate Data

93.4.1 Photolysis

4,6-Dinitro-o-cresol is a moderately acidic substance, pK_a=4.35 (Pearce and Simkins 1968), and will exist substantially as an anion in environmental surface waters. The ultraviolet absorption spectrum of 4,6-dinitro-o-cresol in dioxane exhibits a maximum at about 265 nm which extends out beyond 400 nm (Böhmer et al. 1972). In aqueous sodium hydroxide there is a strong maximum at 372 nm.

Nakagawa and Crosby (1974) report that 4-nitrophenol was degraded in aqueous solutions within a period of 1-2 months when it was exposed to sunlight at a concentration of 200 mg/l. The principal products were hydroquinone and 4-nitrocatechol. A dark, acidic intractable polymer was also produced. Although no specific information was found in the reviewed literature demonstrating that 4,6-dinitro-o-cresol would also be photochemically hydroxylated in an analogous manner, the following mechanistic considerations for this photochemical reacton indicate that, under similar conditions, 4,6-dinitro-o-cresol might be degraded to a mixture of compounds which could possibly include 2-methyl-4-nitrocatechol and 2-methyl-6-nitrohydroquinone.

Nakagawa and Crosby (1974) proposed that the observed reaction products arising from 4-nitrophenol were the result of photonucleophilic displacement reactions involving water or hydroxide ion. This type of reaction mechanism can be easily rationalized for the formation of hydroquinone, but it is probably not valid in the case of 4-nitrocatechol since it is difficult to envision the development of a center of electron deficiency on the unsubstituted carbon atom adjacent to the phenolic group. Suarez et al. (1970) and Günther et al. (1971) have demonstrated that hydroxyl radicals preferentially attack 4-nitrophenol in water at the C-2 and C-4 positions, and that the latter intermediate results in the displacement of the nitro group by a hydroxy group. Even though attack by hydroxyl radical can more easily explain the observed products, it is uncertain whether the concentration of hydroxyl radicals in the experiment of

Nakagawa and Crosby (1974) would have been sufficient to be responsible for the formation of hydroquinone and 4-nitrocatechol.

It has been reported that the ultraviolet irradiation of 4,6-dinitro-o-cresol at 254 nm is without effect (Mitchell 1961). This experiment, however, was conducted by irradiating the compound for 30 minutes after its solution had been applied to a sheet of chromatographic paper which was then dried. The experiment was one of very short duration and the conditions were anhydrous or hypohydrous. For these reasons it is probably not valid to draw any conclusions from this experiment with respect to either the aquatic or terrestrial environment.

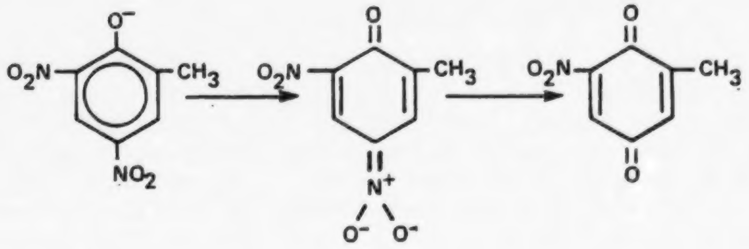
A further photochemical reaction of 4,6-dinitro-o-cresol that must be considered is photoreduction of the nitro groups. As an example, Nakagawa and Crosby (1974) found that the nitro group of nitrofen, a nitroaromatic pesticide, underwent photochemical reduction to amino and azo groups in an aqueous solution that contained 10% methanol. Aromatic nitro groups are, in general, reduced photochemically in the presence of suitable hydrogen donors (Morrison 1969). The log octanol/water partition coefficient of 4,6-dinitro-o-cresol indicates a definite potential for absorption by suspended organic matter. In this way the organic material could serve as a reducing agent in the photoreduction. Massini and Voorn (1967) report that the reduction of 2,4-dinitrophenol by ascorbic acid is sensitized by the presence of chlorophyll and is enhanced further by ferrous ion. Inasmuch as the functional groups of 4,6-dinitro-o-cresol are in the same relative positions as 2,4-dinitrophenol, both compounds may undergo this type of reduction. Intramolecular reduction of 4,6-dinitro-o-cresol involving the methyl group, however, is not as likely a process as it is for the nitrotoluenes because the methyl group is not adjacent to either nitro group (Morrison 1969).

93.4.2 Oxidation

Suarez et al. (1970) and Günther et al. (1971) have demonstrated that hydroxyl radicals attack both 2-nitrophenol and 4-nitrophenol at the C-2 and C-4 positions resulting in the formation of a complex mixture that follows from the generation of isomeric benzosemiquinones. No information was found, however, from which an environmentally relevant rate could be estimated for this reaction. It can be inferred that 4,6-dinitro-o-cresol might be oxidized in an analogous fashion.

93.4.3 Hydrolysis

The covalent bond of a substituent attached to an aromatic ring is usually resistant to hydrolysis because of the high negative charge-density of the aromatic nucleus. Nonetheless, there is a possibility, albeit not specifically substantiated in the reviewed literature, that nitrophenols could undergo hydrolysis while sorbed by clay minerals. Specifically, the water molecules within the clay structure can be highly acidic, and the phenolic group of the sorbed 4,6-dinitro-o-cresol would become more acidic than when the molecule is in aqueous solution due to coordination of the phenolic oxygen atom with the metal cations of the clay. This acidic environment could conceivably lead to the hydrolysis of the 4,6-dinitro-o-cresol anion in a manner similar to the hydrolysis of aci-nitroparaffins (Johnson and Degering 1943).



93.4.4 Volatilization

Although phenol has a significant vapor pressure as a pure substance, nitrophenols can form intermolecular hydrogen bonds in the solid state and can exhibit boiling points much above that of a phenol with the same molecular weight and the absence of nitro groups. Moreover, the vapor pressure of an ionized substance in water is proportional to the percentage of the compound that is not ionized. Under most environmental conditions this would imply that the vapor pressure in water of 4,6-dinitro-o-cresol would be much less than the vapor pressure of the pure substance. (The vapor pressure of pure 3,5-dinitro-o-cresol has been determined to be 5.2×10^{-5} torr at 20°C; Balson 1947). Solution interactions would reduce the vapor pressure even more. Thus, volatilization would probably not be an important process for nitrophenols in general. For example, 4-nitrophenol does not volatilize from a solution of boiling water (Morrison and Boyd 1973).

93.4.5 Sorption

Although the value of the octanol/water partition coefficient indicated by log P = 2.85 suggests a definite potential for sorption of 4,6-dinitro-o-cresol by organic particulates, Zogorski and Faust (1976) have reported that substituted phenolate anions are not easily sorbed from water by lipophilic materials. Although no information was found pertaining to the interaction of this pollutant with clay minerals, there is no reason to believe that it will behave differently from the other nitrophenols (Chang and Anderson 1968). Thus adsorption by clay can be expected to be a significant transport process.

93.4.6 Bioaccumulation

Calculation of the log octanol/water partition coefficient, using the method of Tute (1971), yields a value for log P of 2.85. Within the limits imposed by ionization and toxicity, this compound thus could exhibit a tendency to bioaccumulate. Although no specific information was found in the reviewed literature regarding the bioaccumulation of 4,6-dinitro-o-cresol, the compound cannot be expected to bioaccumulate because of its marked toxicity.

93.4.7 Biotransformation and Biodegradation

Most of the studies of microbial degradation of nitrophenols have concentrated on the isolation of pure cultures which can utilize these pollutants as sources of energy, carbon, or nitrogen (Howard *et al*. 1976). It is questionable whether these studies can be extrapolated to the environment of ambient surface waters since the concentration of the test chemical employed for enrichment of an organism and for obtaining a reasonable amount of cell growth is far above the concentrations generally found in nature.

4,6-Dinitro-o-cresol (DNOC) has been used as a herbicide for several decades and its rate of decomposition in soil has been well studied. DNOC usually disappears from the soil within a few weeks to two months (Gundersen and Jensen 1956; Bruinsma 1960; Hurle and Pfefferkorn 1972). Gundersen and Jensen (1956) isolated an *Arthrobacter* and a *Pseudomonas* that grew on DNOC with the release of nitrite ion. Tewfic and Evans (1966) found that in pure culture *Pseudomonas* degraded DNOC to an aminocresol whereas *Arthrobacter* initially hydroxylated the aromatic ring before catabolism proceeded further.

93.5 Data Summary

Table 93-1 summarizes the aquatic fate data for 4,6-dinitro-o-cresol. This pollutant will probably undergo slow photolytic destruction in ambient surface waters. Volatilization is not thought to be an important transport process but 4,6-dinitro-o-cresol might be strongly sorbed by clay minerals. There is a possibility that 4,6-dinitro-o-cresol could undergo hydrolysis while sorbed onto the clay structure. Although the biotransformation of 4,6-dinitro-o-cresol has been demonstrated, it is uncertain whether biodegradation is an operational fate in ambient surface waters.

Table 93-1

Summary of Aquatic Fate of 4,6-Dinitro-o-Cresol

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis[a]	Slow photooxidation may be the main aquatic fate pathway.	-	-	Low
Oxidation	Displacement of the nitro group by hydroxyl radical may be possible.	-	-	Low
Hydrolysis	Hydrolysis might occur during sorption on a clay surface; insufficient information to assess this pathway.	-	-	Low
Volatilization	Probably not important.	-	-	Low
Sorption	This pollutant should be strongly sorbed by clay minerals.	-	-	Low
Bioaccumulation	Importance is uncertain.	-	-	Low
Biotransformation/ Biodegradation	Probably the main process of removal from agricultural soils; but biodegradation may be very slow in ambient surface waters.	-	-	Low

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a. The predominant environmental process which is thought to determine the fate of the compound.

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SECTION VIII: PHTHALATE ESTERS

Chapter 94

94. PHTHALATE ESTERS:

DIMETHYL PHTHALATE, DIETHYL PHTHALATE, DI-n-BUTYL PHTHALATE, DI-n-OCTYL PHTHALATE, BIS(2-ETHYLHEXYL) PHTHALATE, BUTYL BENZYL PHTHALATE

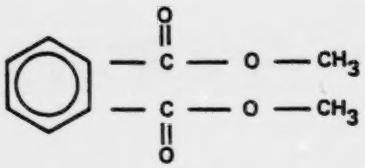
94.1 Statement of Probable Fate

Bis(2-ethylhexyl) phthalate is the most well studied of the phthalate esters. For several of the phthalate esters, however, very little specific data were found, and the aquatic fate of these compounds is to a large extent inferred from data for phthalate esters as a group. Although their solubilities vary from sparingly soluble to moderately soluble, they all are probably readily adsorbed onto suspended particulates and biota and, under certain conditions, are likely to form a water soluble complex with humic substances. Their transport will largely depend on the hydrogeologic conditions of the aquatic system. Volatilization is not considered to be a competitive transport process, with the possible exception of those esters, such as bis(2-ethylhexyl) and butyl benzyl phthalate, that have low solubilities.

A variety of organisms have demonstrated the ability to take up and accumulate phthalate esters; this is probably due to the esters lipophilicity. They have also been shown to become concentrated in animal and human tissues and organs. Mixed microbial systems can degrade phthalate esters under aerobic conditions. Degradation is generally slower under anaerobic conditions and ceases to be effective for bis(2-ethylhexyl) phthalate. A variety of multicellular organisms have demonstrated the ability to biotransform and eliminate phthalate esters. Hydrolysis will occur in the water column, but it may be too slow to be environmentally significant. Bioaccumulation, biotransformation, and biodegradation are probably the important processes determining the aquatic fate of phthalate esters. Based on the data reviewed, however, it is not possible to predict a predominant environmental fate process at this time.

94.2 Identification

Phthalate esters are present in the environment from anthropogenic and perhaps natural sources. As a group, they are widely distributed in the environment, having been found in well and drinking water, oil, soil, air, plants, fish, food, animals, and humans (Mayer *et al.* 1972; Morita *et al.* 1974; Bureau of Foods 1974; Bureau of Foods 1975; Peakall 1975; Giam *et al.* 1978). Residues in surface waters appear to be correlated with drainage from industrial or heavily populated areas (Stalling *et al.* 1973). There is some evidence that phthalate esters might be biosynthesized and occur naturally in certain plants and organisms (Autian 1973; Graham 1973; Peakall 1975). Shackelford and Keith (1976) reported that several phthalate esters have been detected in drinking water and river water. The chemical structures of the phthalate esters discussed in this report follow.

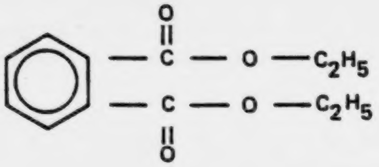


Dimethyl phthalate

CAS NO. 131-11-3
TSL NO. TI 15750

Alternate Names

DMP
1,2-Benzenedicarboxylic acid, dimethyl ester
Phthalic acid dimethyl ester
Methyl phthalate



Diethyl phthalate

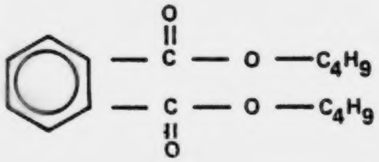
CAS NO. 84-66-2
TSL NO. TI 10500

Alternate Names

DEP
1,2-Benzenedicarboxylic acid, diethyl ester
Ethyl phthalate

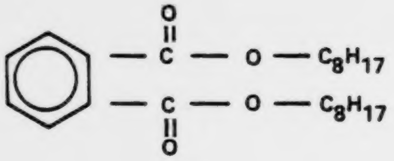
Alternate Names

DBP
o-Benzenedicarboxylic acid, dibutyl ester
Dibutyl phthalate
Benzene-o-dicarboxylic acid, di-n-butyl ester
n-Butyl phthalate



Di-n-butyl phthalate

CAS NO. 84-74-2
TSL NO. TI 08750



Di-n-octyl phthalate

CAS NO. 117-84-0
TSL NO. TI 19250

Alternate Names

DOP
o-Benzenedicarboxylic acid, dioctyl ester
n-Dioctyl phthalate
Octyl phthalate
Dioctyl-o-benzenedicarboxylate

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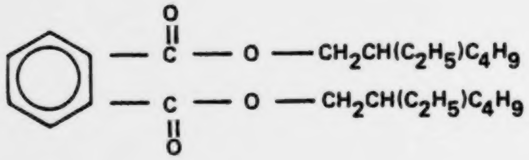
*Di-n-octyl phthalate is sometimes mistakenly reported as its isomer, bis(2-ethylhexyl) phthalate, in the literature.



Bis (2-ethylhexyl) phthalate

CAS NO. 117-81-7
TSL NO. TI 03500

Alternate Names

DEHP
Di(2-ethylhexyl) phthalate
Bis(2-ethylhexyl) ester, phthalic acid
Di-sec-octyl phthalate
Di(2-ethylhexyl) orthophthalate
2-Ethylhexyl phthalate
1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester

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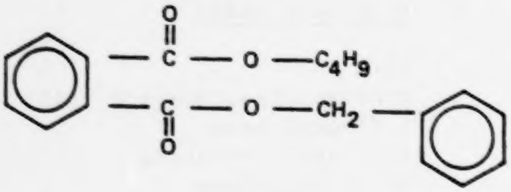
*Bis(2-ethylhexyl) phthalate is sometimes mistakenly reported as its isomer, di-n-octyl phthalate (DOP), in the literature.



Alternate Names

BBP
Benzyl butyl phthalate

Butyl benzyl phthalate

CAS NO. 85-68-7
TSL NO. TH 99900

94.3 Physical Properties

The physical properties of the six phthalate esters are shown in Table 94-1.

Table 94-1

Physical Properties of Phthalate Esters

	dimethyl	diethyl	di-n-butyl	di-n-octyl	bis(2-ethylhexyl)	butyl benzyl
Molecular weight	194.18[a]	222.23[a]	278.34[b]	391.0[a]	391.0[a]	312.0[c]
Melting point	0°C[d]	-40.5°C[a]	-35°C[d]	-25°C[a]	-50°C[a]	-35°C[e]
Boiling point	282°C(760 torr)[d]	298°C(760 torr)[d]	340°C(760 torr)[a]	220°C(4 torr)[a]	386.9°C(5 torr)[a]	377°C(760 torr)[e]
Vapor pressure	<0.01 torr(20°C)[a]	0.05 torr(70°C)[a]	0.1 torr(115°C)[a]	<0.2 torr(150°C)[a]	<0.01 torr(20°C)[a] 2×10^{-7} torr (20°C)[f]	Not available
Solubility	5000 mg/l(20°C)[c] 4000 mg/l(32°C)[g] 4320 mg/l(25°C)[h]	1000 mg/l (32°C)[g] 896(25°C)[h]	13 mg/l(25°C)[h]	3 mg/l(25°C)[h]	0.4 mg/l (25°C)[h] 1.3 mg/l[f]	2.9 mg/l[f]
Log octanol/water partition coefficient	2.12 [i,j]	3.22 [i,j]	5.2 [i,j,k]	9.2 [i,j,k]	8.73 [i,j,k] 5.3[f]	5.8 [i,j,k] 4.8[f]

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a) Patty 1963
b) Weast 1977
c) Fishbein and Albro 1972
d) Verschueren 1977
e) EPA-CHMTADS
f) Hirzy et al. 1978
g) Peakall 1975
h) Determined by Wolfe et al. 1979
i) Calculated as per Leo et al. 1971
j) Calculated by Wolfe et al. 1979
k) Value does not include a correction for the influence of molecular folding because data are not available.

94.4 Summary of Fate Data

94.4.1 Photolysis

No specific information was found concerning the aquatic photolysis of phthalate esters. Since they do not possess significant absorption maxima in the terrestrial sunlight region of the electromagnetic spectrum, phthalate esters are unlikely to undergo direct photochemical reactions in surface waters. Indirect photolysis, involving interaction of the hydroxyl radical with the aromatic ring, is considered to be too slow to be environmentally significant for these compounds (Dorfman and Adams 1973).

94.4.2 Oxidation

No information was found in the reviewed literature to suggest oxidation as an environmental fate process for these compounds.

94.4.3 Hydrolysis

No information was found in the reviewed literature on the environmental hydrolysis of phthalate esters. Based on the data presented below, they are expected to hydrolyze in surface waters, but at such a slow rate that this process may not be environmentally significant under most conditions. The half-lives for the hydrolysis of phthalate esters in general are expected to be on the order of years. The second order rate constant for alkaline hydrolysis of various phthalate esters at a pH of 10-12 and 30°C are shown in Table 94-1 (Wolfe *et al*. 1979). Using the method of Radding *et al*. (1977) to estimate a pseudo-first order rate from a second order rate constant, the corresponding half-lives in water at pH 7 range from 3.2 years for dimethyl phthalate to 2000 years for bis(2-ethylhexyl) phthalate. As expected, the hydrolysis rate is slower for longer chain esters (Fieser and Fieser 1956). The hydrolysis of phthalate esters, as a group, is catalyzed by both acids and bases (Thanassi and Bruice 1966).

94.4.4 Volatilization

No information was found in the reviewed literature to suggest volatilization as a significant transport process for phthalates in natural waters. For example, Saeger and Tucker (1976) observed no significant volatility losses in an experiment with two phthalate esters in activated sludge. In contrast, there is evidence that phthalate esters are slowly volatilized from plastics into air at higher temperatures. Phthalate esters were found in the air and coated on the windows of automobile interiors in hot climates due to volatilization from vinyl furnishings (Autian 1973; Marx 1972; Thomas 1973; Mathur 1974a).

Vapor pressures for phthalate esters are extremely low, contributing much to their thermal stability in plastics. For example, the vapor pressure for dimethyl and diethyl phthalates is less than 0.01 torr at 20°C which is a representative value for phthalates (Patty 1963). Nonetheless, volatilization of some high molecular weight, sparingly soluble organic compounds has been calculated to be surprisingly rapid due presumably to exceptionally high activity coefficients with respect to volatilization from aqueous solution (Mackay and Wolkoff 1973). On this basis, it is possible that the volatilization of sparingly soluble compounds such as bis(2-ethylhexyl) and butyl benzyl phthalate may be a significant process. In one calculation in the literature, however, Branson (1978) estimated that this evaporative half-life for bis(2-ethylhexyl) phthalate from water would be 15 years. In addition, since phthalate esters are readily adsorbed onto particulates (Autian 1973; Peakall 1975) and since volatilization of sorbed compounds normally is slower, volatilization is not considered a likely transport process in natural waters.

94.4.5 Sorption

No specific data for rates of adsorption of phthalate esters onto clay and other particulate materials were found in the reviewed literature. The two transport mechanisms most likely to affect phthalates in the aquatic environment are adsorption onto suspended solids and particulate matter and complexation with natural organic substances.

The calculated log octanol/water partition coefficients for phthalate esters (calculated by the method of Leo *et al*. 1971) range from 2.12 and 3.24 for dimethyl- and diethyl phthalates to 9.22 for bis(2-ethylhexyl) phthalate (Wolfe *et al*. 1979). The coefficients, however, for the longer chain phthalate esters can be anticipated to be in error to some extent due to the unknown contribution of molecular folding. The calculated values indicate that all phthalate esters should be adsorbed onto suspended particulates high in organic matter to a degree in proportion to chain length. This contention is supported by the observation that phthalate esters are commonly found in sediment samples taken from stream bottoms and the sea (Giam *et al*. 1978). Autian (1973) and Peakall (1975) discuss in some detail this process and its significance for the fate of phthalate esters.

Autian (1973) suggests that complexation with natural organic substances may be one mode of transport of phthalate esters from sources of manufacture and use to the aquatic environment. It has been observed that phthalate esters readily interact with the fulvic acid present in humic substances in water and soil. The interaction forms a fulvic acid-phthalate complex which is very soluble in water, thus mobilizing and transporting otherwise insoluble phthalate esters (Ogner and Schnitzer 1970).

94.4.6 Bioaccumulation

Phthalate esters have been identified in living matter, and data collected from field and laboratory studies indicate that a variety of organisms can take up and accumulate them; the majority of the data is for bis(2-ethylhexyl) phthalate (Peakall 1975; Stein *et al*. 1973; Jaeger and Rubin 1973; Sanborn *et al*. 1975; Mayer 1976). Most phthalate esters have a relatively high calculated log octanol/water partition coefficient >2.12 indicating that they are lipophilic. As a result, they are likely to be biosorbed by single and multicellular organisms. Fishbein and Albro (1972) found that phthalate esters migrate from plastic packages into food, especially fatty foods, suggesting that they are highly lipid soluble. Jorque (1973) also reports that phthalate esters partition strongly into the lipids of both plants and animals. There is evidence that they also are degraded by microbiota and metabolized by fish and animals. As a result, phthalate esters are not likely to biomagnify (Autian 1973).

In a model ecosystem, Metcalf *et al*. (1973) reported that bis(2-ethylhexyl) phthalate was rapidly bioaccumulated by a variety of plants and animals. The concentration factors ranged from 130 in fish (*Gambusia affinis*) to 108,000 in mosquito larvae (*Culex*). Sanders *et al*. (1973) reported that aquatic invertebrates (crustacea, scud, glass shrimp, crayfish, water flea, damselfly nymphs, burrowing mayfly, and midge larvae) rapidly take up and accumulate phthalate esters. The rate of accumulation was shown to vary depending on the ester and the organism, as shown in Tables 94-2 and 94-3. Sanders *et al*. (1973) conclude that phthalate esters are not magnified in invertebrates to the same degree as the well-studied organochlorine insectidides.

Tables 94-3 and 94-4 show that after 14 days bis(2-ethylhexyl) phthalate accumulated in invertebrates at levels ranging from 70 to 13,400 times the concentration in water, while di-n-butyl phthalate accumulated 5,000 to 6,700 times. The concentration factor of bis(2-ethylhexyl) phthalate in scud (*Gammarus pseudolimnaeus*) varied inversely with the concentration of bis(2-ethylhexyl) phthalate in water. This finding was confirmed by Mayer (1976) who postulates that a detoxifying enzyme is released by the organism when bis(2-ethylhexyl) phthalate concentrations surpass some unknown threshold value. This causes degradation and elimination of the phthalate ester resulting in lower accumulation factors for the organism.

Marx (1972) reported accumulation factors for phthalate esters concentrated by aquatic organisms to be 350-3900 times the concentration in water after 7 days. Mayer *et al*. (1976) reported that bis(2-ethylhexyl) phthalate is readily accumulated in the fathead minnow exposed to a con-

Table 94-2

SECOND ORDER ALKALINE HYDROLYSIS RATE CONSTANTS FOR PHTHALATE ESTERS AT 30°C IN WATER (pH 10-12). HALF-LIVES WERE CALCULATED FOR pH 7.0[b,c]

Ester	$M^{-1}sec^{-1}$[c]	$t_{1/2}$ (Yrs.)[a,b]
Dimethyl	$(6.9 \pm 0.3) \times 10^{-2}$	3.2
Diethyl	$(1.2 \pm 0.01) \times 10^{-2}$	18.3
Di-n-butyl	$(2.2 \pm 0.6) \times 10^{-2}$	10.0
Bis(2-ethylhexyl)	$(1.1 \pm 0.1) \times 10^{-4}$	2000

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a. Taken from pseudo-first order rate constants at pH 7.0 (Calculated according to Radding et al. 1977).

b. Pseudo-first order rate constant is increased by one order of magnitude for each increase of one pH unit.

c. Wolfe et al. 1979.

Table 94-3

"BIOLOGIC MAGNIFICATION" OF ^{14}C-LABELLED DI-*n*-BUTYL PHTHALATE FROM WATER BY SIX SPECIES OF AQUATIC INVERTEBRATES AT 21°C

ORGANISM	NO. PER SAMPLE	WATER CONCENTRATION (µg/l ± SE [a])	MAGNIFICATION FACTOR [b] AFTER (DAYS)			
			1	3	7	14
Midge larvae *Chironomus plumosus*	18	0.18 ± 0.015	3500	3900	6600	–
Waterflea *Daphnia magna*	180	0.08 ± 0.005	2200	3500	5000	5000
Scud *Gammarus pseudolimnaeus*	18	0.10 ± 0.010	1700	3700	6500	6700
Mayfly *Hexagenia bilineata*	9	0.08 ± 0.001	500	980	1900	–
Glass shrimp *Palaemonetes kadiakensis*	9	0.08 ± 0.001	1500	5000	–	–
Damselfly *Ischnura verticalis*	9	0.10 ± 0.005	1000	1600	2700	–

a Samples taken in triplicate and expressed as mean value ± SE ($P = 0.05$).

b The extracted radioactivity was assumed to be all ^{14}C-labelled di-*n*-butyl phthalate and the concentrations were derived from the original specific activity (1.64 mCi/mmole).

Source: Sanders et al. 1973:86

Table 94-4

"BIOLOGIC MAGNIFICATION" OF ^{14}C-LABELLED DI-ETHYLHEXYL PHTHALATE FROM WATER BY FIVE SPECIES OF AQUATIC INVERTEBRATES

ORGANISM	NO. PER SAMPLE	WATER CONCENTRATION (µg/l ± SE [a])	MAGNIFICATION FACTOR [b] AFTER (DAYS)				
			1	3	7	14	21
Scud *Gammarus pseudolimnaeus*	18	0.1 ± 0.01	2800	5300	13600	13400	–
	18	62.8 ± 3.31[c]	30	100	116	270	260
Midge larvae *Chironomus plumosus*	18	0.3 ± 0.04	2400	2600	3100	–	–
Waterflea *Daphnia magna*	180	0.3 ± 0.04	1200	2500	5200	–	–
Mayfly *Hexagenia bilineata*	9	0.1 ± 0.01	850	1000	2300	–	–
Sowbug *Asellus brevicaudus*	4	1.9 ± 0.12[c]	–	–	80	71	70
	4	62.3 ± 3.31[c]	–	–	20	230	250

a Samples taken in triplicate and expressed as mean value ± SE ($P = 0.05$).

b The extracted radioactivity was assumed to be all ^{14}C-labelled di-ethylhexyl phthalate and the concentrations were derived from the original specific activity (1.84 mCi/mmole).

c Temperature = 25°C.

Source: Sanders et al. 1973:87

centration of 2.5 µg/l in water. After 28 days, the concentration of bis(2-ethylhexyl) phthalate in the fish was 800 times that in water.

Tepper (1973) observed that aquatic organisms were more apt to concentrate phthalate esters than were warm blooded animals. This is supported by Peakall (1974) who found that cold blooded creatures metabolize phthalates much more slowly than warm blooded ones. Nevertheless, phthalate esters have been shown to concentrate in many higher organisms as a result of biosynthesis or diet.

Most animal studies in the reviewed literature were concerned with the exposure of rats to various concentrations and compounds of phthalates. The studies generally support the premise that phthalate esters are lipophilic. Daniel (1973) reported that under continuous exposure to bis(2-ethylhexyl) phthalate, rates demonstrated rapid uptake and accumulation in the liver and fat; a steady state point was reached and there was no evidence of progressive accumulation. Bis(2-ethylhexyl) phthalate was shown to accumulate in the liver, lung, carcass, spleen, and heart of the rat (Jaeger and Rubin 1970; Schulz and Rubin 1973; Jaeger and Rubin 1973). The highest concentrations were reported in the lungs (Autian 1973). Stein _et al._ (1973) reported accumulation of bis(2-ethylhexyl) phthalate in the heart and epididymal fat, but found none in the liver.

Nazir _et al._ (1973) found bis(2-ethylhexyl) phthalate in the heart mitochondria of a cow. Similar findings have been reported for the rat, rabbit, and dog (Autian 1973). It is not clear whether the phthalate esters are biosynthesized or occur as a result of dietary sources and subsequent localization in the heart. These findings are significant because, according to Nazir _et al._ (1973), the phthalate esters could influence the bio-energetics of the myocardial cells.

There is evidence that phthalate esters are also concentrated in human tissue. Jaeger and Rubin (1970) reported bis(2-ethylhexyl) phthalate in the spleen, liver, lungs, and abdominal fat of humans, with the highest concentration occurring in fat.

The data presented herein show that phthalate esters are bioaccumulated by a variety of organisms. There is very little evidence to suggest that any long-term bioaccumulation or biomagnification, such as that demonstrated for some of the persistent organochlorine compounds (PCBs and DDT), will occur for phthalate esters. Phthalate esters, however, are concentrated by higher animals and man in specific tissues and organs. The degree to which biotransformation and biodegradation occur is important in determining the significance of bioaccumulation as an aquatic fate process, but it is not clear to what extent their effect is exerted. Based on the literature reviewed, however, bioaccumulation would seem to definitely have a role in determining the ultimate fate of the studied phthalate esters.

94.4.7 Biotransformation and Biodegradation

There appears to be limited information on the biodegradation and biotransformation of some phthalate esters, and, therefore, their potential for biodegradation and biotransformation is partly inferred from data on phthalate esters as a group. Phthalate esters in the aquatic environment can be metabolized by a variety of organisms and degraded by mixed microbial systems at rates which vary widely, depending on environmental conditions. The literature is replete with data for bis(2-ethylhexyl) phthalate, which is considered, along with di-n-octyl phthalate, to be the least biodegradable phthalate ester (Mathur 1974b). Phthalate esters as a group are thought to undergo microbial degradation much more easily than other well-studied persistent compounds, such as PCBs and DDT (Engelhardt *et al.* 1975). Although environmental levels are high, biotransformation and biodegradation are both important processes in determining the ultimate fate of phthalate esters.

Phthalate esters undergo primary and ultimate biodegradation in different naturally occurring microbial systems by a mechanism which remains unclear, but probably involves some form of enzymic hydrolysis. The rate of degradation can depend on temperature, pH, the presence of oxygen, site, phthalate structure, and probably other variables (Shibko and Blumenthal 1973; Mathur 1974a; Saeger and Tucker 1976). Tepper (1973) suggests that the kinetics of degradation in solution will differ from that in emulsions. Thus, it is not surprising that no generally applicable rates or half-lives were reported in the literature.

Several microorganisms are able to utilize selected phthalate esters as sole sources of carbon and energy. For example, *Serratia*, the ubiquitous saprophytic bacterium known to occur in soil, water, milk and food, was able to utilize bis(2-ethylhexyl) phthalate at substrate levels up to 2.5%; 0.8% bis(2-ethylhexyl) phthalate, in a 25-ml shake culture, was utilized in 3 weeks to the extent of approximately 95% (Mathur and Rouatt 1975). A strain of *Penicillium lilacinuns* was able to biodegrade several phthalate esters. The rates of degradation decreased with increasing number of carbon atoms of the ester groups. For example, di-n-butyl phthalate was completely removed from the culture medium within 30 days, whereas bis-(2-ethylhexyl) and di-n-octyl phthalate were degraded only approximately 50% in 30 days (Engelhard *et al.* 1977).

A strain of *Enterobacter aerogenes* was able to utilize dimethyl phthalate alone at 1000 ppm (Perez *et al.* 1977). Saeger and Tucker (1976) conducted experiments on biodegradation in unacclimated river water and found that phthalate esters generally degraded rapidly; the half-life for butyl benzyl phthalate was less than 2 days, while the rate for bis(2-ethylhexyl) phthalate was slower, with a reported half-life of approximately 4 weeks. The authors conclude that phthalate esters and intermediate degradation products readily undergo ultimate degradation in different mixed microbial systems at concentrations ranging from 1 to 83 mg/l.

Mathur (1974a) found that phthalate esters are biodegraded in soil. He suggests the mechanism to be some form of hydrolysis by specific esterases. Also, he reported that degradation rates decreased at lower temperatures. Johnson and Lulves (1975), in a laboratory study of freshwater hydrosoil, found that ^{14}C-carbonyl-labeled bis(2-ethylhexyl) and di-n-butyl phthalates were degraded with half-lives of approximately 14 days and 1 day, respectively, under aerobic conditions. Under anaerobic conditions, degradation occurred more slowly or not at all. They reported that degradation was due to enzymic action of microorganisms causing initial hydrolysis to a phthalic acid monoester and alcohol. Subsequent oxidative decarboxylation of the exposed carboxyl group probably resulted in 1,2-dihydroxybenzene as a final product. These results were confirmed for degradation of bis(2-ethylhexyl) phthalate by Johnson (1978) in a similar experiment. He concludes that optimal degradation occurs for bis(2-ethylhexyl) phthalate in freshwater hydrosoil under aerobic conditions at pH 7 to 9 and at 20°C.

Saeger and Tucker (1976) reported that phthalate esters were degraded in acclimated activated sludge (aerobic). They postulate the mechanism to be enzymic hydrolysis of the phthalate ester to soluble intermediates, probably a phthalic acid monoester. The authors report primary degradation of 70-78% of bis(2-ethylhexyl) phthalate and 93-99% of butyl benzyl phthalate using an addition-rate of 5 mg/24 hours and 200 mg/24 hours, respectively. Graham (1973) reported 91% degradation of bis(2-ethylhexyl) phthalate and 99% of butyl benzyl phthalate in activated sludge under controlled conditions and a continuous feeding rate of 5 mg/48 hrs. The work of Thom and Agg (1975) generally supports the biodegradability of phthalate esters by biological sewage treatment provided suitable acclimation can be achieved. It should be noted, however, that in actual field analysis of sewage sludge, bis(2-ethylhexyl) phthalate residues were commonly found at 176 to 884 µg/kg (dry weight) (Johnson et al. 1977). This may be due to the large quantities of phthalate esters in raw sewage, rather than the inefficiency of activated sludge processes in degrading phthalate esters.

A number of studies report that fish and aquatic life can metabolize phthalate esters. In a model ecosystem, Sanborn et al. (1975), found di-n-octyl phthalate to be degraded and metabolized by a variety of aquatic organisms. After 14 days of continuous exposure to 0.1 µg/l of bis(2-ethylhexyl) phthalate, a fathead minnow was placed in freshwater where a half-life of 12.2 days was reported for biotransformation and elimination (Mayer 1976). In a similar study, Mayer et al. (1972) found that after 10 days nearly all bis(2-ethylhexyl) phthalate was eliminated from scud (*Gammarus pseudolimnaeus*). Sanders *et al*. (1973) found a half-life of 3 days for bis(2-ethylhexyl) phthalate in the water flea (*Daphnia magna*). They noted that metabolism increased as the water concentration of phthalate esters increased, suggesting that enzymic action was stimulated and thereby increased the transformation rate.

Stalling *et al*. (1973) studied the metabolism of di-n-butyl phthalate and bis(2-ethylhexyl) phthalate *in vivo* and *in vitro* in the channel catfish. The authors reported the metabolic pathway to be enzymatic hydrolysis to a monophthalate and alcohol. One of the metabolites, mono-2-(ethylhexyl) phthalate, is reported to be 100 times more toxic than phthalic acid or bis(2-ethylhexyl) phthalate (Carter 1975). Stalling *et al*. (1973) also reported the formation of glucuronides of these compounds and indicated that two distinct enzymic systems in microsomes controlled the metabolism of phthalate esters. They found different rates of transformation for different phthalate structures as evidenced by degradation rates for di-n-butyl phthalate being 16 times faster than those for bis(2-ethylhexyl) phthalate.

Most studies of rats cite hydrolysis *in vivo* with subsequent metabolite oxidation as the principal metabolic pathway for phthalate esters. Jaeger and Rubin (1973) indicate that the limited mammalian data seem to show that at least most ingested phthalate esters are rapidly metabolized. Metabolism was again shown to depend on phthalate structure by Jaeger and Rubin (1970) when, in a study of a perfused rat liver, they found that bis(2-ethylhexyl) phthalate did not degrade while shorter chain phthalate esters did. Albro and Moore (1974), in a study of rat urinary metabolites of phthalate esters, reported a di-n-butyl phthalate metabolic pathway of enzymatic hydrolysis to a phthalic acid monoester and alcohol, and a subsequent α and β oxidation of the carboxyl terminated metabolites.

Studies, using rat gastro-intestinal contents, *in vitro* indicate that most short chain phthalate esters are hydrolyzed to monoesters in the small intestine before adsorption. Acute toxicity appeared to be correllated with the formation of the metabolite and not to the di-ester itself, and the enzymes responsible for the hydrolysis appeared to be of animal origin (Rowland *et al*. 1977). Homogenates of intestinal and hepatic tissue taken from several species, including man, also hydrolyzed phthalate diesters with rates inversely related to chain length (Lake *et al*. 1977).

The data presented herein show that biotransformation and biodegradation are important fate processes for phthalate esters as a group and would seem to definitely have a role in determining their ultimate fate. The degree to which these processes will dominate other fate mechanisms will depend on many factors and is not clear at this time.

94.4.8 Microcosm Studies, Field Studies, and Modelling

In order to understand the behavior of a compound in an ecosystem, it is instructive and sometimes necessary to use an evaluative model. One such model, EXAMS, (Exposure Analysis Modeling System developed at EPA's Athens Laboratory) simulates the expected environmental fate and transport processes using the physical, chemical and biological fate data (particularly kinetic) obtained from laboratory studies (Smith et al. 1978). The major limitation to a model of this type is the establishment of a data base for the correlation. Where the ratio of independent processes vary significantly, only an order of magnitude accuracy is required and estimation of various parameters is adequate. In systems where competing processes are suggested, more accurate values obtainable only by laboratory measurements are desirable. Wolfe et al. (1979) employed EXAMS to study the type of behavior expected by various phthalate esters. Although the details are beyond the scope of this report, a summary of the results for dimethyl and bis(2-ethylhexyl) phthalate is given in Table 94-5. These two compounds represent the extreme in both structure and physical properties and thus would be expected to exhibit the most divergent behavior in an aquatic ecosystem.

The simulation predicts that, for phthalates esterified with short-chain alkyl groups, chemical and biochemical transformations will compete favorably in the ecosystems which have long retention times (i.e., in ponds or lakes). For phthalates esterified with larger alkyl groups, such as bis(2-ethylhexyl) phthalate, transformation processes are slow and transport will predominate in all cases. Transport will be the dominant process for all phthalate esters entering a river regardless of chain length. As expected, phthalate esters with alkyl chains of intermediate length exhibit intermediate behavior, with diethyl and dibutyl phthalates more closely resembling dimethyl phthalate and di-n-octyl resembling bis(2-ethylhexyl) phthalate.

If input into the various ecosystems remains at a constant level, the concentrations of the short chain esters can be expected to approach a steady state. The concentrations of the longer chain esters, in particular bis(2-ethylhexyl) phthalate, would, according to the model, continue to increase in aquatic ecosystems. If input were stopped altogether, the level would be expected to decrease relatively quickly in the former but persist for an undetermined length of time in the latter. The oceans may be considered the ultimate sink for phthalate esters introduced into unimpeded rivers.

94.5 Data Summary

Summaries of the data discussed above are presented in Tables 94-6.1 through 94-6.6. Only limited, published environmental fate information was

Table 94-5

HALF-LIVES AND PERCENTAGE OF LOAD FOR THE CHEMICAL, BIOLOGICAL, AND EXPORT PROCESSES FOR DMP AND DEHP IN FIVE SIMULATED ECOSYSTEMS (Wolfe et al. 1979)

Compound	Ecosystem	Chemical		Biological		Export	
		$t_{1/2}$	%Load	$t_{1/2}$	%Load	$t_{1/2}$	%Load
DMP[1,3]	River	2.6×10^4 hr	0.04	111 hr	9.4	11.5 hr	90
	Pond	2.7×10^3 hr	0.47	13 hr	97	693 hr	1.9
	Eutrophic Lake	2.7×10^3 hr	0.90	27 hr	98	5.2×10^3 hr	0.51
	Oligitrophic Reservoir	4.9×10^3 hr	0.96	27 hr	99	5.3×10^3 hr	0.47
DEHP[2,3]	River	8.2×10^4 dy	0.01	1.5×10^6 dy	0.0	4.7 dy	99.9
	Pond	2.2×10^4 mo	0.23	1.0×10^5 mo	0.05	51 mo	99
	Eutrophic Lake	3.7×10^3 mo	1.7	3.5×10^4 mo	0.18	64 mo	98
	Oligitrophic Lake	505 mo	1.7	1.3×10^5 mo	0.05	8.9 mo	98
	Reservoir	3.2×10^3 mo	1.9	2.9×10^4 mo	0.2	62.5 mo	98

---

[1] Dimethyl phthalate

[2] Bis(2-ethylhexyl) phthalate

[3] Ester concentration at time zero is 0.1 mg/l.

found for most of the phthalates, and some of the summaries are inferred from data on phthalate esters as a group. Although the global dispersion of phthalate esters is probably due to vaporization during use or waste disposal, the principal aquatic transport mechanisms are probably adsorption onto suspended particulates and biota and complexation with humic substances. Bioaccumulation, biotransformation, and biodegradation are all considered to make a substantial contribution to fate processes, but the degree of influence on the ultimate fate of phthalate esters is unclear. Phthalate esters appear to be more readily biodegradable than other well studied persistent compounds, such as PCBs and DDT.

Table 94-6.1

Summary of Aquatic Fate of Dimethyl phthalate

Environmental Process[a]	Summary Statement[b]	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Probably does not undergo direct photolysis in surface waters; indirect photolysis might occur, but would be too slow to compete with other processes.	-	-	Low
Oxidation	Not considered a competitive fate process.	-	-	Low
Hydrolysis	Will hydrolyze very slowly under most conditions; not considered a competitive process.	-	3.2 years[c] (Calculated)	High
Volatilization	Not considered as important a transport process as adsorption.	-	-	Medium
Sorption	Sorption onto suspended particulates and biota, and complexation with humic substances are probably the most important transport mechanisms.	-	-	Medium
Bioaccumulation	A variety of organisms take up and accumulate phthalate esters. Probably lipophilic. Bioaccumulation is considered an important fate process.	-	-	Low
Biotransformation/ Biodegradation	Phthalate esters are degraded under most conditions and can be metabolized by multicellular organisms; biodegradation is considered an important fate process.	-	-	Medium

---

a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. Very little environmental fate data specific to dimethyl phthalate were found; the summary statement, to a large extent, is made from data reviewed for phthalate esters as a group.

c. Wolfe et al. 1979 and Radding et al. 1977.

Table 94-6.2

Summary of Aquatic Fate of Diethyl phthalate

Environmental Process[a]	Summary Statement[b]	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Probably does not undergo direct photolysis in surface waters; indirect photolysis might occur, but would be too slow to compete with other processes.	-	-	Low
Oxidation	Not considered a competitive fate process.	-	-	Low
Hydrolysis	Will hydrolyze very slowly under most conditions. Not considered a competitive process.	-	~18.3 years[c] (Calculated)	High
Volatilization	Not considered as important a transport process as adsorption.	-	-	Low
Sorption	Sorption onto suspended particulates and biota, and complexation with humic substances are probably the most important transport mechanisms.	-	-	Low
Bioaccumulation	A variety of organisms take up and accumulate phthalate esters; probably lipophilic. Bioaccumulation is considered an important fate process.	-	-	Low
Biotransformation/ Biodegradation	Phthalate esters are degraded under most conditions and can be metabolized by multicellular organisms; biodegradation is considered an important fate process.	-	-	Low

---

a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. Very little environmental fate data specific to diethyl phthalate were found; the summary statement, to a large extent, is made from data reviewed for phthalate esters as a group.

c. Wolfe et al. 1979 and Radding et al. 1977.

Table 94-6.3

Summary of Aquatic Fate of Di-n-butyl phthalate

Environmental Process[a]	Summary Statement[b]	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Probably does not undergo direct photolysis in surface waters; indirect photolysis might occur, but would be too slow to compete with other processes.	-	-	Low
Oxidation	Not considered a competitive fate process.	-	-	Low
Hydrolysis	Will hydrolyze very slowly under most conditions; not considered a competitive process.	-	~10 years[c] (Calcualted)	High
Volatilization	Not considered as important a transport process as adsorption.	-	-	Medium
Sorption	Sorption onto suspended particulates and biota, and complexation with humic substances are probably the most important transport mechanisms.	-	-	Medium
Bioaccumulation	A variety of organisms take up and accumulate di-n-butyl phthalate and phthalate esters; probably lipophilic. Bioaccumulation is considered an important fate process.	-	-	Medium
Biotransformation/ Biodegradation	Di-n-butyl phthalate and phthalate esters are degraded under most conditions and can be metabolized by multicellular organisms; biodegradation is considered an important fate process.	-	-	Medium

---

a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. Environmental fate data specific to di-n-butyl phthalate were supplemented with data reviewed for phthalate esters as a group.

c. Wolfe _et_ _al_. 1979 and Radding _et_ _al_. 1977.

Table 94-6.4

Summary of Aquatic Fate of Di-n-octyl phthalate

Environmental Process[a]	Summary Statement[b]	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Probably does not undergo direct photolysis in surface waters; indirect photolysis might occur, but would be too slow to compete with other processes.	-	-	Low
Oxidation	Not considered a competitive fate process.	-	-	Low
Hydrolysis	Will hydrolyze very slowly under most conditions; not considered a competitive process.	-	Not available[c]	High
Volatilization	Not considered as important a transport process as adsorption.	-	-	Medium
Sorption	Sorption onto suspended particulates and biota, and complexation with humic substances are probably the most important transport mechanisms.	-	-	Medium
Bioaccumulation	A variety of organisms take up and accumulate di-n-octyl phthalate and phthalate esters; probably lipophilic. Bioaccumulation is considered an important fate process.	-	-	Medium
Biotransformation/ Biodegradation	Di-n-octyl phthalate and phthalate esters are degraded under most conditions and can be metabolized by multicellular organisms; biodegradation is considered an important fate process.	-	-	Medium

---

a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. Environmental fate data specific to di-n-octyl phthalate were supplemented with data reviewed for phthalate esters as a group.

c. Not available but structural considerations and comparison to other phthalates suggest a very long half-life.

Table 94-6.5

Summary of Aquatic Fate of Bis(2-ethylhexyl) phthalate

Environmental Process[a]	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Probably does not undergo direct photolysis in surface waters; indirect photolysis might occur, but would be too slow to compete with other processes.	-	-	Low
Oxidation	Not considered a competitive fate process.	-	-	Low
Hydrolysis	Will hydrolyze very slowly under most conditions; not considered a competitive process.	-	2000 years[b] (Calculated)	High
Volatilization	Not considered as important a transport process as adsorption.	-	-	Medium
Sorption	Sorption onto suspended particulates and biota, and complexation with humic substances are probably the most important transport mechanisms.	-	-	High
Bioaccumulation	A variety of organisms take up and accumulate bis(2-ethylhexyl) phthalate; probably lipophilic. Bioaccumulation is considered an important fate process.		-	High
Biotransformation/ Biodegradation	Bis(2-ethylhexyl) phthalate is degraded under most conditions and can be metabolized by multicellular organisms; biodegradation is considered an important fate process.		~4 weeks[c]	High

---

a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. Wolfe et al. 1979 and Radding et al. 1977.

c. Reported by Saeger and Tucker (1976) in a laboratory study of river water.

Table 94-6.6

Summary of Aquatic Fate of Butyl Benzyl Phthalate

Environmental Process[a]	Summary Statement[b]	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Probably does not undergo direct photolysis in surface waters; indirect photolysis might occur, but would be too slow to compete with other processes.	-	-	Low
Oxidation	Not considered a competitive fate process.	-	-	Low
Hydrolysis	Will hydrolyze very slowly under most conditions; not considered a competitive process.	-	Not available[c]	Low
Volatilization	Not considered as important a transport process as adsorption.	-	-	Low
Sorption	Sorption onto suspended particulates and biota, and complexation with humic substances are probably the most important transport mechanism.	-	-	Low
Bioaccumulation	A variety of organisms take up and accumulate phthalate esters; probably lipophilic. Bioaccumulation is considered an important fate process.	-	-	Low
Biotransformation/ Biodegradation	Phthalate esters are degraded under most conditions and can be metabolized by multicellular organisms; biodegradation is considered an important fate process.	-	-	Low

---

a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. Very little environmental fate data specific to butyl benzyl phthalate were found; the aquatic fate, to a large extent, is inferred from data reviewed for phthalate esters as a group.

c. Not available but structural considerations and comparison to other phthalates suggest a very long half-life.

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SECTION IX: POLYCYCLIC AROMATIC HYDROCARBONS

Chapters 95-98

95. POLYCYCLIC AROMATIC HYDROCARBONS: ACENAPHTHENE, ACENAPHTHYLENE, FLUORENE, NAPHTHALENE

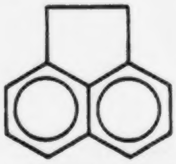
95.1 Statement of Probable Fate

The aquatic fates of four polycyclic aromatic hydrocarbons having two aromatic rings are discussed in this chapter. Very little data specific to these compounds were found; their aquatic fate, therefore, is inferred for the most part from data summarized for polycyclic aromatic hydrocarbons in general. The results of the data summary suggest that these compounds, which vary in aqueous solubility from 1.9 mg/l for fluorene to 34 mg/l for naphthalene, will adsorb strongly onto suspended particulates and biota and that their transport will be determined largely by the hydrogeologic condition of the aquatic system. Polycyclic aromatic hydrocarbons dissolved in the water column will probably undergo direct photolysis at a rapid rate. The ultimate fate of those which accumulate in the sediment is believed to be biodegradation and biotransformation by benthic organisms.

95.2 Identification

Polycyclic aromatic hydrocarbons are present in the environment from both natural and anthropogenic sources. As a group, they are widely distributed in the environment, having been detected in animal and plant tissue, sediments, soils, air and surface water (Radding et al. 1976); Shackelford and Keith (1976) report that naphthalene has been detected in surface waters, finished drinking water, industrial effluents, ambient river water, well water, and ground water. Fluorene has been found in both industrial effluents and river water, while acenaphthene and acenaphthylene have been detected in surface water and drinking water, respectively.

The chemical structures of the polycyclic aromatic hydrocarbons discussed in this section are shown below.

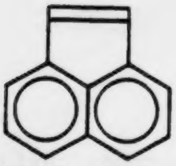


Acenaphthene

CAS NO. 83-32-9
TSL NO. None assigned

Alternate Names

None Assigned

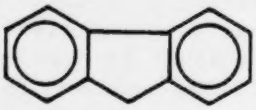


Acenaphthylene

CAS NO. 208-96-8
TSL NO. None assigned

Alternate Names

None Assigned

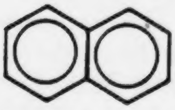


Fluorene

CAS NO. 86-73-7
TSL NO. None assigned

Alternate Names

2,3-Benzidene
Diphenylenemethane



Naphthalene

CAS NO. 91-20-3
TSL NO. QJ 05250

Alternate Names

Moth Balls
Tar Camphor
Naphthene

95.3 Physical Properties

The general physical properties of the polycyclic aromatic hydrocarbons containing 2 aromatic rings discussed in this chapter are as follows.

	Acenaphthene	Acenaphthylene	Fluorene	Naphthalene
Molecular weight	154.21[a]	152.21[a]	116.15[a]	128.19[b]
Melting point	96°C[a]	92°C[a]	116-117°C[a]	80.55[b]
Vapor pressure (20°C)	10^{-3}-10^{-2} torr[c]	10^{-3}-10^{-2} torr[c]	10^{-3}-10^{-2} torr[c]	.0492 torr[b]
Solubility in water (25°C)	3.42 mg/l[d]	3.93 mg/l[e]	1.98 mg/l[e] 1.69 mg/l[h]	34.4 mg/l[e] 31.7 mg/l[h]
Log octanol/water partition coefficients	4.33[f]	4.07[f]	4.18[f]	3.37[g]

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a) Weast 1977.
b) Cleland and Kingsbury 1977.
c) Estimated, based on data for structurally similar compounds.
d) Eganhouse and Calder 1976.
e) Mackay and Shiu 1977.
f) Calculated as per Leo _et_ _al_. 1971.
g) Radding _et_ _al_. 1976.
h) May and Wasik 1978.

95.4 Summary of Fate Data

95.4.1 Photolysis

Most polycyclic aromatic hydrocarbons absorb solar radiation strongly at wavelengths above the solar cutoff (~300 nm) and may, therefore, undergo direct photolysis or photooxidation (Radding et al. 1976). The review by Radding et al. (1976) indicates that direct photolysis in the aqueous environment may be an important fate process for these compounds, especially naphthalene, since its aqueous solubility is relatively high (34.4 mg/l at 25°C).

Several authors studying the photolysis of polycyclic aromatic hydrocarbons have stated that singlet oxygen is the oxidant and that the reaction products are quinones (NAS 1972; Stevens and Algar 1968). Studies performed by Smith et al. (1978) on benzo[a]pyrene and benzo[a]anthracene show that photolysis is rapid for these compounds when they are in aqueous solution. Using the procedure of Zepp and Cline (1977), Smith et al. (1978) report calculated half-lives (midday photolysis in winter) of 1.2 hours for benzo[a]pyrene and 1 to 2 hours for benzo[a]anthracene.

Southworth (1977) observed that anthracene dissolved in distilled water was rapidly degraded when exposed to natural sunlight, with a photolytic half-life of about 35 minutes under midday sunlight (midsummer, 35°N latitude). Using the Zepp and Cline (1977) procedure, Southworth (1977) predicts that, in shallow waters, anthracene will exhibit a photolytic half-life of 4.8 hours under average winter solar conditions at 35°N latitude.

In consideration of the aqueous solubilities of these compounds, photolysis appears to be potentially a major fate process. Contrasting with this conclusion is the work of Lee and Anderson (1977) who report that photolysis of naphthalene did not occur when the compound was added to a controlled ecosystem. These results, however, are not conclusive since other fate processes were affecting levels of naphthalene in the laboratory ecosystem. Therefore, at this point the role of photolysis as a fate process is in question.

95.4.2 Oxidation

In natural water the principal oxidizing species are: (1) alkylperoxy ($RO_2\cdot$) and hydroperoxy ($HO_2\cdot$) radicals produced by photolytic cleavage of trace carbonyl compounds or from enzymatic sources, and (2) singlet oxygen. The role of singlet oxygen was discussed above; it is considered to be the major oxidant species involved in the direct photolysis of polycyclic aromatic hydrocarbon molecules.

Several qualitative studies of free-radical oxidation of polycyclic aromatic hydrocarbons have been reported (Tipson 1965; NAS 1972) and are summarized by Radding et al. (1976). The rates of free radical oxidation by $RO_2\cdot$ vary among specific compounds (Mahoney 1965) and also depend on the concentration of $RO_2\cdot$ radicals, which Radding et al. (1976) estimate to be a 10^{-10} molar steady-state concentration under average daily illumination in natural water systems. Half-lives for the reaction of $RO_2\cdot$ radical with anthracene, benzo[a]pyrene, and perylene have been calculated to be 1600, 9900, and 1600 days, respectively (Radding et al. 1976). Although rate constants were not reported for the polycyclic aromatic hydrocarbons discussed in this section, it appears probable that the half-lives for their oxidation by the $RO_2\cdot$ radical are similarly long and that faster processes must determine their probable aquatic fate.

Chlorine and ozone, when used in disinfecting drinking water, are strong oxidants which can chemically react with any polycyclic aromatic hydrocarbon present in the water to form quinones. Perry and Harrison (1977) studied the removal by chlorination of 8 polycyclic aromatic hydrocarbons including fluorene from water. Concentrations ranged from 30-860 ng/l, amounts normally encountered in raw waters. With 2.2 mg/l free chlorine, pH 6.8 and 20°C only 25% of fluorene was degraded after 25 minute exposure while 50% of pyrene was degraded after 20 minutes. Decreased pH, and increased temperature both increased the rate of degradation. Data summarized by Radding et al. (1976) indicate that benzo[a]pyrene will have an initial ten-minute half-life when exposed to a 0.5 mg/l solution of chlorine in water (Trakhtman and Manita 1966). From observations of Il'nitskii et al. (1968), Radding et al. (1976) calculated half-lives of selected polycyclic aromatic hydrocarbons (pyrene, benzo[a]pyrene, benzo[a]anthracene) with ozone in water to be approximately one minute. While these data are not specific to all of the polycyclic aromatic hydrocarbons discussed here, oxidation by chlorine and ozone may be a significant fate process when these oxidants are available in sufficient quantity.

95.4.3 Hydrolysis

Polycyclic aromatic hydrocarbons do not contain groups amenable to hydrolysis. Hydrolysis, therefore, is not thought to be a significant fate process (Radding et al. 1976).

95.4.4 Volatilization

An actual volatilization rate is necessary to assess the importance of this transport process. Several authors have suggested ways to estimate volatilization rates of compounds from water using theoretical considerations (Mackay and Wolkoff 1973; Mackay and Leinonen 1975; Tsivoglou 1967). These methods, however, are still being developed, require a large amount of physical data not usually available, and still may not predict the actual volatilization rate. With the exception of naphthalene, measured volatilization rates for the compounds described herein were not found in the literature, and an assessment of volatilization as a transport process from data measured for other polycyclic aromatic hydrocarbons discussed herein is only speculative.

All compounds with two rings and discussed in this chapter, have the highest vapor pressure of the polycyclic aromatic hydrocarbons. On that basis, volatilization could be a significant process for them. Lee (1975), while not carrying out a rate experiment per se, observed a 50 percent loss of naphthalene from a marine environment when the compound was measured as part of an oil spill. The rate of loss was dependent on air and water temperatures, wind speed, and wave action.

In a laboratory study of a model stream 1.0 m in depth, Southworth (1979) measured the volatilization rates of several polycyclic aromatic hydrocarbons containing from 2 to 5 rings. He found for example that the volatilization rate in general decreases as the vapor pressure decreases, both of which appear to be inversely related to the number of aromatic rings, and that the volatilization rate is highly dependent upon the mixing rates within both the water and air columns. Polycyclic aromatics containing fewer aromatic rings such as naphthalene and anthracene are more sensitive to mixing within the water column than those containing a greater number of aromatic rings such as benz[a]pyrene and benz[a]anthracene. For example, the volatilization half-life for naphthalene increased 7.5 times compared to 1.4 for benz[a]pyrene following a 10 fold increase in stream flow velocity. The volatilization rate was less sensitive to changes in wind velocity but still increased up to 5 times for a 10 fold increase in velocity and the half-times for volatilization of naphthalene, anthracene, benz[a]anthracene and benz[a]pyrene with maximum wind velocities (4 m/sec) and stream current velocities (1 m sec) were 3,2,16,150 and 430 hours respectively. Since these values represent the theoretically expected maximum (not taking into account physical factors which slow evaporation such as sorption), Southworth concludes that the rate of vaporization of polycyclic aromatics with 4 or more rings will be insignificant under all conditions and the evaporation of lower molecular compounds such as naphthalene may be substantial only in a clear, rapidly flowing shallow stream.

Smith et al. (1978) measured the volatilization rate of benzo[a]pyrene and benzo[a]anthracene using the method of Hill et al. (1976). The volatilization half-lives of benzo[a]pyrene and benzo[a]anthracene in a rapidly-stirred aqueous solution were 22 and 89 hours, respectively. These half-lives are relatively long when compared to those related to direct photolysis. Smith et al. (1978) further state that when benzo[a]pyrene and benzo[a]anthracene are sorbed onto sediments, volatilization of the sorbed compound is presumed to be very slow. These half-lives are close to a factor of 5 less than those of Southworth 1979. The reasons are currently obscure.

Southworth (1977), using the mass transfer equation of Liss and Slater (1974), predicts a volatilization half-life of 300 hours for anthracene under quiescent conditions in a water body one meter in depth. The predicted half-life is reduced to about 18 hours when the system is well stirred, so that one can assume thorough and instaneous mixing throughout the water column and the presence of a concentration gradient only at the surface. This number compares well with the experimental number obtained by Southworth 1979. As discussed previously, these assumptions are difficult to justify for environmental conditions, and any similar predictions for other compounds are high speculative.

Based upon available information, volatilization is unlikely to be an important transport process for polycyclic aromatic hydrocarbons. Volatilization of some high molecular weight, sparingly soluble organics, however, has been shown to be surprisingly rapid due to exceptionally high activity coefficients (Mackay and Leinonen 1975) and one cannot discount a similar behavior for polycyclic aromatic hydrocarbons.

95.4.5 Sorption

The data reviewed did not reveal specific partition coefficients for ancenaphthene, acenaphthylene, fluorene, and naphthalene onto suspended particulate matter or biota. They are, however, widely distributed in the environment and are transported as adsorbed matter on particulates suspended in air or water (NAS 1972; Radding et al. 1976). The calculated log octanol/water partition coefficient for the polycyclic aromatic hydrocarbons discussed in this chapter range from 3.37 for naphthalene (Radding et al. 1976) to 4.33 for acenaphthene calculated acording to Leo et al. 1971). Although these coefficients are not extremely large, they indicate that these compounds should be strongly adsorbed onto suspended particulate matter, especially particulates high in organic content.

Benzo[a]pyrene and benzo[a]anthracene, with log octanol/water partition coefficients of 6.31 and 5.61, respectively, show rapid partitioning onto suspended matter as reported by Smith et al. (1978). These authors report partition coefficients (Kp) of 150,000 for benzo[a]pyrene and 21,000 for benzo[a]anthracene between water and sediment containing 5 percent organic carbon, and indicate that sorption onto sediments is strongly correlated with the organic carbon levels in sediments. Using a one-compartment model which simulates river conditions, Smith et al. (1978) predict that 83 percent of benzo[a]pyrene and 71 percent of benzo[a]anthracene will be sorbed onto the suspended solids present in the simulated river. The experimental work performed by Smith et al. (1978) with benzo[a]anthracene and benzo[a]pyrene shows that both are strongly sorbed onto bacterial cells as well as suspended abiotic particulate matter.

In a similar experiment Southworth (1977) showed that anthracene (log octanol/water partition coefficient of 4.45) was sorbed by inorganic sediments and suspended organic particulates. The organic particulates used were autoclaved yeast cells. A partition coefficient (solids/water) of approximately 25,000 was observed, which is indicative of a strong tendency for anthracene to be bioadsorbed. Sorption by inorganic particulates was less and resulted in a partition coefficient of 1600.

Since naphthalene has the lowest log octanol/water partition coefficient of the polycyclic aromatic hydrocarbons discussed herein, it will not adsorb as strongly as compounds like benzo[a]pyrene. Recent work by Lee and Anderson (1977) show that naphthalene will accumulate in sediments up to two orders of magnitude greater than the concentration in the overlying water. In this particular case the transport roles of volatilization and adsorption may, in fact, be quite competitive, with the dominant process probably being directly related to environmental conditions. However, for most polycyclic aromatic hydrocarbons, adsorption is probably the dominant aquatic transport process.

95.4.6 Bioaccumulation

A large number of polycyclic aromatic hydrocarbons have been identified in living matter, and data collected from field and laboratory studies indicate that organisms throughout the phylogenetic scale can incorporate and metabolize polycyclic aromatic hydrocarbons (Radding et al. 1976). With the exception of naphthalene no specific data on the bioaccumulation of the compounds in this section were available, and the limited data on bioaccumulation of naphthalene (as described below) were difficult to assess because of the lack of controls used during the experimentation.

Measurements of naphthalene content in zooplankton (copepods) exposed to high concentrations show that significant uptake can occur (Lee and Anderson (1977). Lee et al. (1972) examined the uptake of C^{14}-naphthalene by the common marine mussel when exposed to an initial concentration range of 32 to 100 μg/l. After 4 hours, mussels had accumulated as much as 10 percent (3.0-10.0 μg) of the naphthalene present, with the gills showing the highest concentration. Anderson (1974) exposed sheepshead minnows (Cyprinodon variegatus) to 1.0 μg/l of naphthalene in sea water for four hours and determined the tissue level of naphthalene to be 60 ppm. After 29 hours in a clean, uncontaminated environment, the tissue concentration dropped to 10 ppm. Lee's work provides evidence for the rapid accumulation of naphthalene, within minutes of exposure, and concentration in the liver where it is rapidly metabolized. The major metabolite identified by Lee et al. (1972) was cis-1,2-dihydro-1,2-dihydroxy-naphthalene.

Southworth et al. (1978) determined the bioaccumulation potential of seven polycyclic aromatic hydrocarbons including naphthalene, anthracene, phenanthrene, pyrene, 9-methylanthracene, benz[a]anthracene and perylene in Daphnia pulex. All were rapidly taken up with naphthalene and anthracene reaching an equilibrium within 2 and 6 hours respectively and benz[a]anthracene in 24 hours. The equilibrium concentration factors increased dramatically with increasing molecular weight ranging from 100 for naphthalene to 10,000 for benz[a]anthracene. The calculated n-octanol-/water partition coefficients were found to be good predictors of bioaccumulation potential in Daphnia. The rapid bioaccumulation suggests that body burdens in zooplankton will follow closely the aqueous concentration of polycyclic aromatics and not be dependent upon food chain.

Roubal et al. (1977) studied the uptake of selected aromatic compounds by young Coho salmon and found that the uptake increased in the order anthracene > naphthalene > benzene regardless of the mode of application. The findings indicate also that the aromatic hydrocarbons in key organs increased in relation to the number of benzenoid rings and the octanol/water partition coefficients.

Jerina (1970) determined that rat liver microsomes can metabolize (in vitro) naphthalene to 1-hydroxynaphthalene, trans-1,2-dihydro-1,2-didroxynaphthalene, and cis-(1,2-dihydro-2-hydroxynaphthalene) glutathione.

Bioaccumulation data for other polycyclic aromatic hydrocarbons shows that, although they are rapidly bioaccumulated to levels comparable to their log P (octanol/water partition coefficient), they are also rapidly metabolized and eliminated (excreted) from the organism as conjugated metabolites (Anderson 1978; Hase and Hites 1976; Lee et al. 1972; Niaussat and Auger 1970; Scaccini-Cicatelli 1966; Southworth 1977). Bioaccumulation, especially in vertebrate organisms, is considered to be short-term, and is probably quite unlike the long-term bioaccumulation that has been demonstrated for some of the more persistent chlorinated organics (e.g., polychlorinated biphenyls). Thus, bioaccumulation of the polycyclic aromatics discussed in this section is not considered an important fate process.

95.4.7 Biotransformation and Biodegradation

The degradation and metabolism of polycyclic aromatic hydrocarbons and the identification of their metabolites are known from studies conducted with bacteria and mammals, and summarized by the National Academy of

Sciences (1972) and Radding et al. (1976). In mammals, the major metabolities of these compounds are hydroxylated derivatives and epoxides (Sims 1970); degradation by mammals, however, is considered incomplete with the parent compound and the metabolites being excreted via the urinary system (Evans et al. 1965).

Bacteria have been shown to utilize some polycyclic aromatic hydrocarbons compounds as a sole carbon source for growth, and evidence summarized by Radding et al. (1976) suggest that bacteria can degrade these compounds much more completely than mammals. Evidence for bacterial degradation comes from studies conducted on only a few polycyclic aromatic hydrocarbons, however.

Naphthalene, one of the compounds containing two aromatic rings discussed in this chapter, is probably the most easily biodegraded polycyclic aromatic hydrocarbon. Lee and Ryan (1976) measured microbial degradation rates as high as 4 μg/l liter^{-1}day^{-1} for naphthalene in Skidaway River water. Lee and Anderson (1977) report that after 1 day of exposure to natural river microbial populations, the amount of naphthalene was reduced to 50 percent owing to adsorption and microbial degradation. Lee and Anderson (1977) measured decay rates, at a depth of 5-10 meters, which range from 0.04 to 3.3 μg l^{-1}day^{-1}. Vennberg (1977) observed that 50 percent of naphthalene present in a test enclosure was converted to CO_2 by microorganisms after one day.

The biotransformation of naphthalene, discussed previously, is relatively rapid and incomplete in vertebrate organisms resulting in conjugated metabolites which are rapidly eliminated. The results obtained with other polycyclic aromatics, though not directly applicable to the compounds containing two aromatic rings may, (when coupled with the results for naphthalene) indicate the probable fate of acenaphthene, acenaphthylene and fluorene. For example, Evans et al. (1965) report that phenanthrene is metabolized by soil Pseudomonads to 1,2-dihydroxynaphthalene via several steps involving hydroxylated intermediates. Data presented by Fedoseeva et al. (1968), Lorbacher et al. (1971), Shabad (1968), and others demonstrate that soil microbes are capable of degrading certain polycyclic aromatic hydrocarbons, primarily 3,4-benzopyrene, anthracene, and phenanthrene, and that the rate and degree of degradation is greatest when the soil and its microbial population have acclimated to the polycyclic aromatic hydrocarbon. Soil systems are known to provide much better conditions for biodegradation than aquatic systems. Poglazova et al. (1972) report that indigenous bacteria of power plant and coke oven wastewater effluents contaminated with 3,4-benzopyrene metabolized less than 15 percent of the compound.

Data presented by Smith et al. (1978) seem to indicate that long-term exposure of microbes is necessary before a bacterial population is capable of degrading polycyclic aromatic hydrocarbons. Their work with three sets of experimental conditions used in attempting to develop enrichment cultures to degrade benzo[a]pyrene and benzo[a]anthracene failed to yield systems capable of significant biodegradation. Smith et al. (1978) surmise that there is a natural preselection and induction process that occurs under natural conditions and that their experimental conditions did not allow for the proper induction period.

Herbes and Schwall (1978) determined the microbial transformation of several polycyclic aromatic hydrocarbons including naphthalene, anthracene, benz[a]anthracene and benz[a]pyrene in both pristine and petroleum contaminated sediment. Half-times for degradation ranged from 5 hours for naphthalene to 280 hours for anthracene, 7,000 hours for benz[a]anthracene and 21,000 hours for benz[a]pyrene in petroleum contaminated sediment. Degradation rates were on the other hand 10-400 times slower in pristine sediment demonstrating clearly the importance of adaptation and acclimation in microbial degradation of polycyclic aromatic hydrocarbons. It appears also that the ease of transformation even by the acclimated microorganisms is inversely related to the number of rings, with some, such as benz[a]-pyrene, being almost totally resistant to transformation. Since no microorganisms have been isolated that are capable of using 4 or 5 ringed compounds as sole carbon sources, it is most likely that they are being cometabolized with simpler and relatively more degradable compounds.

Southworth (1977) reports the rate of microbial degradation of anthracene to be 0.0612 hr^{-1} with a corresponding half-life of 11.3 hours, in water collected from a small stream that was known to be chronically affected by industrial effluents that contained anthracene. Southworth (1977) summarized his findings by stating that the persistence of anthracene in natural waters under summer conditions of temperature and illumination appears to be primarily determined by the fate processes of photolysis and degradation by microorganisms suspended in the water column. Furthermore, he reports that in large, deep (5 m), slow moving rivers, such as the upper Ohio, depth and turbidity would act to reduce the importance of photolysis, making microbial activity the major fate process. The applicability of his conclusion to other polycyclic aromatic hydrocarbons in general is not known. It is presently unclear why Southworth's rates are on the order of 20 x faster than those of Herbes and Schwall (1978) since both experiments were done in petroleum contaminated water and sediment.

Biodegradation is probably slower in the aquatic system than in the soil, and biodegradation may be much more important in those aquatic systems which are chronically affected by contamination. Biodegradation and biotransformation may be the dominant fate processes in the aquatic environment for naphthalene in particular, and probably for all the other compounds discussed in this chapter.

95.5 Data Summary

The results of the data review indicate that, under most environmental conditions, the dominant aquatic transport process for the polycyclic aromatic hydrocarbons will be adsorption onto suspended particulates. The role of volatilization is unknown but under certain conditions (e.g., water agitation) it could be competitive with adsorption. The ultimate fate of naphthalene and possibly other polycyclic aromatics appears to be biodegradation by microorganisms and metabolism (biotransformation) by multicellular organisms. The summary statements presented in Tables 95-1.1 through 95-1.4 are, for the most part, taken from fate data which apply to polycyclic aromatic hydrocarbons in general.

Table 95-1.1

Summary of Aquatic Fate of Acenaphthene

Environmental Process[a]	Summary Statement[b]	Rate	Half-Life ($t_{1/2}$)	Confidence of Data[c]
Photolysis	Dissolved portion may undergo rapid photolysis.			
Oxidation	Oxidation of PAH by $RO_2\cdot$ radical is a slow process; not a significant process.			
Hydrolysis	PAHs do not contain groups amenable to hydrolysis.			
Volatilization	Is probably not as important as adsorption as a transport process.			
Sorption[d]	Measured adsorption coefficients for PAH and suspended solids are high; movement via sediment is considered an important transport process for PAH.			
Bioaccumulation	A short-term process; PAHs with less than 4 rings are readily metabolized and long-term partitioning into biota is not a significant fate process.			
Biotransformation/ Biodegradation	PAHs with less than 4 rings are degraded by microbes and are readily metabolized by multicellular organisms; biodegradation is considered the ultimate fate process.			

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. Very little environmental fate data specific to acenaphthene were found; the summary is made from data reviewed for PAHs as a group.

c. Data on acenaphthene are not sufficient to permit confidence ranking. The confidence of the data reviewed for PAHs in general ranges from low to high.

d. Because the solubility of this compound is relatively high, 50 percent or more may exist in true solution under conditions of normal sediment loading (Southworth 1979).

Table 95-1.2

Summary of Aquatic Fate of Acenaphthylene

Environmental Process[a]	Summary Statement[b]	Rate	Half-Life ($t_{1/2}$)	Confidence of Data[c]
Photolysis	Dissolved portion may undergo rapid photolysis.			
Oxidation	Oxidation of PAH by $RO_2\cdot$ radical is a slow process; not a significant process.			
Hydrolysis	PAHs do not contain groups amenable to hydrolysis.			
Volatilization	Is probably not as important as adsorption as a transport process.			
Sorption[d]	Measured adsorption coefficients for PAH and suspended solids are high; movement via sediment is considered an important transport process for PAH.			
Bioaccumulation	A short-term process; PAHs with less than 4 or 5 rings are readily metabolized and long-term partitioning into biota is not a significant fate process.			
Biotransformation/ Biodegradation	PAHs with less than 4 rings are degraded by microbes and are readily metabolized by multicellular organism; biodegradation is probably the ultimate fate process.			

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. Very little environmental fate data specific to acenaphthylene were found; the summary statement is made from data reviewed for PAHS as a group.

c. Data on acenaphthylene are not sufficient to permit confidence ranking. The confidence of the data reviewed for PAHS in general ranges from low to high.

d. Because the solubility of this compound is relatively high, 50 percent or more may exist in true solution under conditions of normal sediment loading (Southworth 1979).

Table 95-1.3

Summary of Aquatic Fate of Fluorene

Environmental Process[a]	Summary Statement[b]	Rate	Half-Life ($t_{1/2}$)	Confidence of Data[c]
Photolysis	Dissolved portion may undergo photolysis.			
Oxidation	Oxidation of PAH, by RO_2 radical is a slow process; not a significant process.			
Hydrolysis	PAHs do not contain groups amenable to hydrolysis.			
Volatilization	Is probably not as important a transport process as adsorption.			
Sorption[d]	Measured adsorption coefficients for PAH suspended solids are high; movement via sediment is considered an important transport process for PAH.			
Bioaccumulation	A short-term process; PAHs with less than 4 rings are readily metabolized and long-term partitioning into biota is not a significant fate process.			
Biotransformation/ Biodegradation	PAHs with less than 4 rings are degraded by microbes and are readily metabolized by multicellular organisms; biodegradation is probably the ultimate fate process.			

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. Very little environmental fate data specific to fluorene were found; the summary statement is made from data reviewed for PAHs as a group.

c. Data on fluorene are not sufficient to permit confidence ranking. The confidence of the data reviewed for PAHs in general ranges from low to high.

d. Because the solubility of this compound is relatively high, 50 percent or more may exist in true solution under conditions of normal sediment loading (Southworth 1979).

Table 95-1.4

Summary of Aquatic Fate of Naphthalene

Environmental Process[a]	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Dissolved portion may undergo rapid photolysis.	-	-	Medium
Oxidation	Oxidation of naphthalene by RO_2 radical is slow; not a significant process.	-	-	Medium
Hydrolysis	Naphthalene does not contain groups amenable to hydrolysis.	-	-	High
Volatilization	Role is unknown; could be competitive with adsorption under highly stirred conditions.	-	-	Low
Sorption	Measured adsorption coefficients for PAH and suspended solids are high; movement via sediment is considered an important transport process for PAH.	-	-	Medium
Bioaccumulation	A short-term process; napthalene is readily metabolized and long-term partitioning into biota is not a significant fate process.	-	-	High
Biotransformation/ Biodegradation	Naphthalene is degraded by microbes and readily metabolized by multi-cellular organisms; biodegradation is probably the ultimate fate process.	0.04 - 3μg $l^{-1}day^{-1}$	~1 day	Medium

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[a] There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

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96. POLYCYCLIC AROMATIC HYDROCARBONS: ANTHRACENE, FLUORANTHENE, PHENANTHRENE

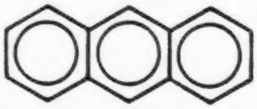
96.1 Statement of Probable Fate

Three polycyclic aromatic hydrocarbons each containing three aromatic rings are discussed in this chapter. Very few data were found and their aquatic fate is inferred for the most part from data summarized for polycyclic aromatic hydrocarbons in general. The results of the data summary, which includes theoretical and empirical evidence, suggests that anthracene, fluoranthene and phenanthrene, compounds only sparingly soluble in water (0.073, 0.26 and 1.29 mg/l respectively), will be adsorbed onto suspended particulates and biota and that their transport will be largely determined by the hydrogeologic conditions of the aquatic system. That portion dissolved in the water column may undergo direct photolysis at a rapid rate. The ultimate fate of the polycyclic aromatic hydrocarbon which accumulate in the sediment is believed to be biodegradation and biotransformation by benthic organisms.

96.2 Identification

Polycyclic aromatic hydrocarbons are present in the environment from anthropogenic and perhaps natural sources. As a group, they are widely distributed in the environment, having been detected in animal and plant tissue, sediments, soils, air and surface water (Radding et al. 1976). Shackelford and Keith (1976) report that anthracene, fluoranthene and phenanthrene have been detected in finished drinking water, industrial effluents, and ambient river water.

The chemical structures of the polycyclic aromatic hydrocarbons containing three aromatic rings and discussed in this chapter are shown below.

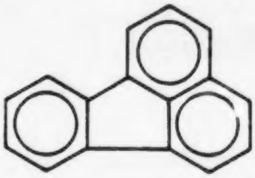


Anthracene

CAS NO. 120-12-7
TSL NO. CA 93500

Alternate Names

Paranaphthalene
Green Oil
Tetra Olive NZG

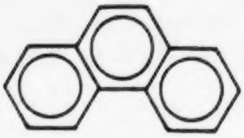


Fluoranthene

CAS NO. 206-44-0
TSL NO. LL 40250

Alternate Names

Benzo [j,k]fluorene
Idryl



Phenanthrene

CAS NO. 85-0108
TSL NO. SF 71750

Alternate Names

Phenanthren

96.3 Physical Properties

The general physical properties of anthracene, fluoranthene and phenanthrene are as follows:

	Anthracene	Fluoranthene	Phenanthrene
Molecular weight	178.23[a]	202.26[b]	178.23[a]
Melting point	216°C[a]	111°C[c]	101°C
Vapor Pressure (20°C)	1.95×10^{-4} torr[a]	10^{-6}-10^{-4} torr[d]	6.8×10^{-4} torr[a]
Solubility in water (25°C)	0.045 mg/l[g] 0.073 mg/l[e]	0.26 mg/l[e]	1.00 mg/l[g] 1.29 mg/l[e]
Log octanol/water partition coefficients	4.45[a]	5.33[f]	4.46[a]

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a) Radding et al. (1976)
b) Weast (1977)
c) Cleland and Kingsbury (1977)
d) Estimated, based on data for structurally similar compounds.
e) Mackay and Shiu (1977)
f) Calculated as per Leo et al. (1971)
g) May and Wasik (1978)

96.4 Summary of Fate Data

96.4.1 Photolysis

Polycyclic aromatic hydrocarbons absorb solar radiation strongly at wavelengths above the solar cutoff (~300 nm) and may, therefore, undergo direct photolysis or photooxidation (Radding et al. 1976). Although no data were found for phenanthrene, and only limited data for anthracene and fluoranthene, the review of Radding et al. 1976 indicates that photolysis in the aquatic environment may be an important fate process for these compounds. Several authors studying the photolysis of polycyclic aromatic hydrocarbons have stated that singlet oxygen is the oxidant and that the reaction products are quinones (NAS 1972; Stevens and Algar 1968). Studies performed by Smith et al. (1978) on benzo[a]pyrene and benzo[a]anthracene show that photolysis is rapid for these compounds when they are in aqueous solution. Using the procedure of Zepp and Cline (1977), Smith et al. (1978) report calculated half-lives (midday photolysis in winter) of 1.2 hours for benzo[a]pyrene and 1 to 2 hours for benzo[a]anthracene. The absolute reactivity of anthracene toward singlet oxygen is reported by Radding et al. (1976) to be $2x10^6$ liter $mol^{-1}sec^{-1}$.

Southworth (1977) observed that anthracene in distilled water was rapidly degraded under exposure to natural sunlight, with a photolysis half-life of about 35 minutes under a midday sunlight in midsummer at 35° north latitude. Using the Zepp and Cline (1977) procedure, Southworth (1977) predicts that, in shallow waters, anthracene will exhibit a photolytic half-life of 4.8 hours under average winter solar conditions at 35°North latitude and about 1.6 hours in the summer. Southworth (1977) also reports that the absorption of light by dissolved and suspended matter will act to reduce photolysis rates considerably. He reports a 19-fold increase in the photolytic half-life of anthracene in a turbid water system containing about 50 mg/l of clay suspension.

The role of photolysis is dependent on the aquatic system. Southworth (1977) states that in large, deep (5 meters), slow-moving rivers, such as the upper Ohio, depth and turbidity would act to reduce the importance of photolysis. In a relatively deep, transparent water body he estimates that photolysis accounts for 18% of the rate of anthracene removal.

Lee et al. (1978) report that photochemical oxidation appears to be an important process in the destruction of oil slicks which contain fluoranthene and, based on their laboratory studies, it appears that fluoranthene is subject to photochemical oxidation when present in slicks or surface waters.

In summary, photolysis appears to be an important aquatic fate process competitive with other processes under certain conditions. For fluoranthene and phenanthrene, the role of direct photolysis is hard to assess at this time. When present as part of an oil slick, fluoranthene may degrade by photochemical oxidation but when sorbed onto suspended particulate (a most likely occurance), it may not be degraded by photolysis at a rate rapid enough to be competitive with other fate processes.

96.4.2 Oxidation

In natural water the principal oxidizing species are: (1) alkylperoxy ($RO_2\cdot$) and hydroperoxy ($HO_2\cdot$) radicals generated by photolytic cleavage of trace carbonyl compounds or from enzymatic sources, and (2) singlet oxygen. The role of singlet oxygen was discussed above; it is considered to be the major oxidant species involved in the direct photolysis of polycyclic aromatic hydrocarbon molecules.

Several qualitative studies of free-radical oxidation of polycyclic aromatic hydrocarbons have been reported (NAS 1972; Tipson 1965) and are summarized by Radding *et al*. (1976). The rates of free radical oxidation by $RO_2\cdot$ vary among specific compounds (Mahoney 1965) and also depend on the concentration of $RO_2\cdot$ radicals, which Radding *et al*. (1976) estimate to be a 10^{-10} molar steady-state concentration under average daily illumination in natural water systems. Half-lives for the reaction of $RO_2\cdot$ radical with anthracene, benzo[a]pyrene, and perylene at 60°C have been calculated to be 1600, 9900, and 1600 days, respectively (Radding *et al*. 1976). Radding *et al*. (1976) report an oxidative half-life of 8×10^6 days for phenanthrene when reacted with the $RO_2\cdot$ radical at 60°C; this corresponds to a rate coefficient of 0.01 liter $mol^{-1}sec^{-1}$. The differences in reaction rates of polycyclic aromatic hydrocarbons with $RO_2\cdot$ are probably as large as that found for any group of organic compounds. For all of the polycyclic aromatic hydrocarbons noted above, the half-lives for free-radical oxidations are so long even at 60°C that other, faster processes are more effective in removing these compounds from the environment. It appears probable that the oxidation of anthracene and fluoranthene will also be too slow to be competitive with other processes.

Chlorine and ozone, when used in disinfecting drinking water, are strong oxidants which can chemically react with any polycyclic aromatic hydrocarbon present in the water to form quinones. Data summarized by Radding *et al*. (1976) indicate that benzo[a]pyrene will have an initial ten-minute half-life when exposed to a 0.5 mg/l solution of chlorine in water (Trakhtman and Manita 1966). From observations of Il'nitskii *et al*. (1968), Radding *et al*. (1976) calculated half-lives of selected compounds (pyrene, benzo[a]pyrene, benzo[a]anthracene) with ozone in water to be approximately one minute. While these data are not specific to anthracene, fluoranthene or phenanthrene, oxidation by chlorine and ozone may be a significant fate process when these oxidants are available in sufficient quantity.

96.4.3 Hydrolysis

Polycyclic aromatic hydrocarbons in general do not contain groups amenable to hydrolysis. Hydrolysis, therefore, is not thought to be a significant fate process (Radding et al. 1976).

96.4.4 Volatilization

To assess the importance of volatilization as a transport process for any compound in natural water, a volatilization rate is necessary. Several authors have suggested ways to estimate volatilization rates of compounds from water using theoretical considerations (Mackay and Wolkoff 1973; Mackay and Leinonen 1975). These methods, however, are still being developed, require a large amount of physical data not yet available for the compound, and still may not accurately estimate the actual volatilization rate. A measured volatilization rate for fluoranthene and phenanthrene was not found in the literature, and an assessment of volatilization as a transport process, from data measured for other polycyclic aromatics, is only speculative at this time.

Southworth (1977), using the mass transfer equation of Liss and Slater (1974), predicts a volatilization half-life of 300 hours for anthracene under quiescent conditions in a water body one meter in depth. The predicted half-life is reduced to about 19 hours when the system is well-stirred, so that one can assume thorough and instantaneous mixing throughout the water column and the presence of a concentration gradient only at the surface. Southworth estimates that volatilization accounts for 21 percent toward the removal of anthracene from a very shallow (0.25 meter), clear stream.

In a laboratory study of a model stream 1.0 m in depth Southworth (1979) measured the volatilization rates of several polycyclic aromatic hydrocarbons containing from 2 to 5 rings. He found for example that the volatilization rate in general decreases as the vapor pressure decreases both of which are inversely related to the number of aromatic rings, and that the volatilization rate is highly dependent upon the mixing rates within both the waters and associated air columns. Polycyclic aromatics containing fewer aromatic rings such as naphthalene and anthracene are also more sensitive to mixing within the water column than those containing a greater number of aromatic rings such as benzo[a]pyrene and benzo[a]anthracene. For example the volatilization half-life for naphthalene increased 7.5 times compared to 1.4 for benzo[a]pyrene following a 10 fold increase in stream flow velocity. The volatilization rate was less sensitive to change in wind velocity but still increased up to 5 times for a 10 fold increase in velocity and the half-time for volatilization of naphthalene, anthracene, benzo[a]anthracene and benzo[a]pyrene with maximum wind velocity (4 m/sec) and stream current velocity (1 m/sec) were 3.2, 16, 150 and 430 hours respectively. Since these values represent the theoretically expected maximum (not taking into account physical factors which slow evaporation such as sorption) Southworth (1979) concludes that the rate of vaporization of polycyclic aromatics with 4 or more rings will be insignificant under all conditions and the evaporation of lower molecular weight compounds such as naphthalene may be substantial only in a clean, rapidly flowing stream.

Smith et al. (1978) measured the volatilization rate of benzo(a)pyrene and benzo(a)anthracene using the method of Hill et al. (1976). The volatilization half-lives of benzo(a)pyrene and benzo(a)anthracene in a rapidly-stirred aqueous solution were 22 and 89 hours, respectively. These half-lives are relatively long when compared to direct photolysis. Smith et al. (1978) further state that when benzo(a)pyrene and benzo(a)anthracene are sorbed onto sediments, volatilization of the sorbed compound is presumed to be very slow.

Lee et al. (1978) report that hydrocarbons below C_{15} (b.p. < 270°C) volatilize in a few days from an oil slick. In a controlled ecosystem experiment, they predict a rapid loss of naphthalene due to volatilization; hydrocarbons in the C_{15}-C_{25} range, such as anthracene, fluoranthene and phenanthene, are volatilized from an oil slick only to a limited extent. The work by Lee et al. (1978) is not quantitative since rates of volatilization were not measured or estimated.

Volatilization of some high molecular weight, sparingly soluble organics has been shown to be surprisingly rapid owing to exceptionally high activity coefficients (Mackay and Wolkoff 1973). While it cannot be discounted that polycyclic aromatic hydrocarbons will have similarly high activity coefficients, the available data suggest that volatilization will not be an important transport process for polycyclic aromatic hydrocarbons in general.

96.4.5 Sorption

Polycyclic aromatic hydrocarbons are widely distributed in the environment and are transported as adsorbed matter that is suspended on particulates in air or water (NAS 1972; Radding et al. 1976;). The calculated log octanol/water partition coefficients of 4.45, 5.33 and 4.44 for anthracene, fluoranthene and phenanthrene, respectively (Radding et al. 1976) indicate that the compound should be strongly adsorbed onto suspended particulate matter, especially particulates high in organic content (Leo et al. 1971).

Southworth (1977) showed that anthracene (log octanol/water partition coefficient of 4.45) was sorbed by inorganic sediments and suspended organic particulates. The organic particulates used were autoclaved yeast cells. A distribution coefficient (ratio of the concentration of anthracene between solids/water) of approximately 25,000 was observed, which is indicative of a strong tendency for anthracene to be bioadsorbed. Sorption by inorganic particulates was less and resulted in a distribution coefficient of 1600. The data reviewed did not reveal specific partition coefficients of fluorenthene and phenanthrene onto suspended particulate matter or biota.

Southworth (1977) also considered the sedimentation rate in evaluating the adsorption of anthracene. He states that the rate of removal of anthracene by adsorption and subsequent sedimentation of particulates is determined by the extent of adsorption and rate of sedimentation. Calculated removal rates for anthracene range from 7.2×10^{-3} hr^{-1} ($t_{1/2}$ = 96 hours) for clay particles to $1.44 \times 10^{-3} hr^{-1}$ ($t_{1/2}$ = 481 hours) for silt particles. In calculating these removal rates, Southworth (1977) used a sedimentation rate of 8.4 cm/yr.

Whether sedimentation rates are competitive with other processes such as volatilization, photolysis, and degradation depends upon the hydrologic conditions. Sedimentation is for the most part slower than photolysis and degradation but may be competitive with volatilization. For example, in the presence of a strong water current, sedimentation rates are likely to be far slower, and hence adsorption-sedimentation will not be a significant process for the net removal of anthracene from the water column. Southworth (1977) carefully states, that his data does not necessarily mean that anthracene will not accumulate in sediments. In fact, the coupling of adsorption rates to bedded sediments and microbial degradation rates within the sediments yields a predicted sediment concentration of anthracene greater than 80 percent of equilibrim values.

Benzo[a]pyrene and benzo[a]anthracene, with log octanol/water partition coefficients of 6.31 and 5.61, respectively, show rapid partitioning onto suspended matter as reported by Smith _et al_. (1978). These authors report partition coefficients (Kp) of 150,000 for benzo[a]pyrene and 21,000 for benzo[a]anthracene between water and sediment containing 5 percent organic carbon, and indicate that sorption onto sediments is strongly correlated with the organic carbon levels in sediments. Using a one-compartment model which simulates river conditions, Smith _et al_. (1978) predict that 83 percent of benzo[a]pyrene and 71 percent of benzo[a]anthracene will be sorbed onto the suspended solids present in the simulated river. The experimental work performed by Smith _et al_. (1978) with benzo[a]anthracene and benzo[a]pyrene shows that both are strongly sorbed onto bacterial cells as well as suspended abiotic particulate matter.

These data indicate that the compounds cited above, and probably polycyclic aromatics as a group, will accumulate in the sediment and biota portions of the aquatic environment and that adsorption is probably the dominant aquatic transport process for these compounds in general.

96.4.6 Bioaccumulation

A large number of polycyclic aromatic hydrocarbons have been identified in living matter, and data collected from field and laboratory studies indicate that organisms throughout the phylogenetic scale can incorporate and metabolize polycyclic aromatic hydrocarbons (Radding *et al.* 1976). Specific data on the bioaccumulation of anthracene, fluoranthene and phenanthrene were limited, and conclusions are somewhat based on these compounds as a group. High (calculated) log octanol/water partition coefficients (log P) of 4.45, 5.33 and 4.46 respectively, together with the theoretical and empirical data that compounds with high log P values tend to accumulate in biota (Neely *et al.* 1974), indicate that these compounds probably will be bioaccumulated.

Southworth *et al.* (1978) determined the bioaccumulation potential of seven polycyclic aromatic hydrocarbons including naphthalene, anthracene, phenanthrene, pyrene, methylanthracene, benzo[a]anthracene and perylene in *Daphania pulex*. All were rapidly taken up with naphthalene and anthracene reaching an equilibirum within 2 and 6 hours respectively and benzo[a]anthracene in 24 hours. The equilibirum concentration factors increased dramatically with increasing molecular weight ranging from 100 for naphthalene to 10,000 for benzo[a]anthracene. The calculated n-octanol/-water partition coefficients were found to be good predictors of the bioaccumulation potential in *Daphnia*. The rapid bioaccumulation suggests that body burdens in 700 plankton will follow closely the aqueous concentration of polycyclic aromatics and not be dependent upon food chain.

Lee *et al.* (1978) report the uptake of anthracene and fluoranthene by zooplankton in a controlled ecosystem study. On day 4 of the study, the copepod *Pseudocalanus minutus*, contained 1.4 μg/g of fluoranthene and 3.3 μg/g anthracene, more than in the water column but less than that reported in the bottom sediments. After 9 days, the concentration of these compounds was below detectable levels, (<0.1 μg/g) owing to the ability of the zooplankton to degrade and discharge the compound.

Oysters suspended in an oil-treated enclosure rapidly took up oil hydrocarbons, including anthracene and fluoranthene, a component of the oil (Lee *et al.* 1978). When the oysters were placed in non-contaminated water, depuration of the hydrocarbons resulted. Naphthalenes were rapidly released whereas fluoranthene and anthracene were released much slower. Based on these depuration experiments, Lee et al. (1978) calculate a half-life for depuration of 3 and 5 days for anthracene and fluoranthene respectively, assuming exponential discharge.

The sorption of benzo[a]pyrene and benzo[a]anthracene onto bacterial cells was found to be rapid with a partition coefficient (cell/-water) of approximately 10^4 (Smith et al. 1978). Niaussat and Auger (1970) report that biota in a lagoon contaminated with 3,4-benzopyrene and perylene accumulated both compounds, and that accumulation was greater in those species occupying a niche near the top of the food chain. Freshwater worms (Tubifex sp.), when exposed to 3,4-benzopyrene, were shown to accumulate the compound with increasing exposure followed by slow depuration when placed in uncontaminated water (Scaccini-Cicatelli 1966).

Roubal, et al. 1977 studied the uptake of selected aromatic compounds by young Coho Salmon and found that the uptake increased in the order anthracene > naphthalene > benzene regardless of the mode of application. The findings indicate that the aromatic hydrocarbons in key organs increased in relation to the number of benzenoid rings and the octanol/water partition coefficients.

Using anthracene, Southworth (1977) conducted laboratory bioaccumulation studies on zooplankton (Daphnia and fish (Pimephales). He found that bioaccumulation in both species was rapid, and that equilibrium concentration factors attained by each organism were comparable. The rapid bioaccumulation suggests that body burdens of anthracene in zooplankton will closely follow aqueous anthracene concentrations, with food chain magnification not likely to be significant due to the rapid direct uptake of anthracene from water by fish.

Using radiolabeled naphthalene, Lee et al. (1972) determined that, for various marine invertebrates, naphthalene is accumulated in tissue within hours of exposure and stored in the liver, where it is rapidly metabolized. Naphthalene and its metabolites are then transferred to the bile and eventually excreted.

The data discussed above support the premise that, although all polycyclic aromatic hydrocarbons are rapidly bioaccumulated, those with 4 or less rings in particular are also rapidly metabolized and eliminated (excreted) from the organism. Bioaccumulation, therefore, is considered to be short-term, and is probably unlike the long-term bioaccumulation that has been demonstrated for some of the more persistent chlorinated organics (e.g., PCB's, DDT).

96.4.7 Biotransformation and Biodegradation

The degradation and metabolism of polycyclic aromatic hydrocarbon compounds and the identification of their metabolites are known from studies conducted with bacteria and mammals, as summarized by the National Academy of Sciences (1972) and Radding et al. (1976). In mammals, the major metabolites of these compounds are hydroxylated derivatives and epoxides (Sims 1970); degradation by mammals, however, is considered incomplete with the parent compound and the metabolites being excreted via the urinary system (Evans et al. 1965).

Bacteria have been shown to utilize some polycyclic aromatic hydrocarbons as a sole carbon source for growth, and evidence summarized by Radding et al. (1976) suggest that bacteria can degrade them much more completely than mammals. Evidence for bacterial degradation comes from studies conducted on only a few compounds; data specific to anthracene, fluoranthene and phenanthrene were very limited and the general conclusions are, therefore, based on biodegradation studies conducted for several selected polycyclic aromatic hydrocarbons.

Herbes and Schwall (1978) determined the microbial transformation of several polycyclic aromatic hydrocarbons including naphthalene, anthracene, benzo[a]anthracene and benzo[a]pyrene in both pristine and petroleum contaminated sediment. Half-times for degradation ranged from 5 hours for naphthalene to 280 hours for anthracene, 7,000 hours for benzo[a]anthracene and 21,000 hours for benzo[a]pyrene in petroleum contaminated sediments. Degradation rates were, on the other hand, 10-400 times slower demonstrating clearly the importance of adaptation and acclimation in microbial degradations of polycyclic aromatic hydrocarbons. It appears also that the ease of transformation even by the acclimated microorganisms is inversely related to the number of rings, with some such as benzo[a]pyrene being almost totally resistant to transformation. Since no microorganisms have been isolated that are capable of using 4 or 5 ringed compounds as a sole carbon source, it is most likely that they are being cometabolized with simpler and relatively more degradable compounds.

The microbial degradation of polycyclic aromatic hydrocarbons was also studied by Groenewegen and Stolp (1975). Their data show that tricyclic aromatic hydrocarbons are capable of being degraded by microbes "but such degradation is not known for higher polycyclic hydrocarbons." They further report that organic compounds which are difficult to degrade are sometimes co-oxidized by microbes although these organisms cannot use them as their sole source of carbon. Using a mixed "cocktail" of polycyclic aromatic hydrocarbons, Groenewegen and Stolp (1975) report that phenanthrene, pyrene, 1,2-benzanthracene, and 3,4-benzopyrene were degraded significantly. Fluorene and fluoranthene were only somewhat degraded and chrysene was not degraded to any measurable degree. The role of microbial degradation is probably significant in determining the aquatic fate of phenanthrene.

Barnsley (1975) reports that biodegradation of fluoranthene occurs most rapidly in cultures in the stationary phase, is heat sensitive, requires oxygen, and is enhanced in the presence of cyanide. The maximum rate of fluoranthene metabolism by *Pseudomonas* (NClB9816) observed by Barnsley (1975) was 2.2×10^{-3} μmol hr^{-1} mg^{-1} bacterial protein.

Data presented by Smith *et al*. (1978) seem to indicate that long-term exposure of microbes is necessary before a bacterial population is capable of degrading polycyclic aromatic hydrocarbons. Their work with three sets of experimental conditions used in attempting to develop enrichment cultures to degrade benzo[a]pyrene and benzo[a]anthracene failed to yield systems capable of significant biodegradation. Smith *et al*. (1978) surmise that there is a natural preselection and induction process that occurs under natural conditions and that their experimental conditions did not allow for the proper induction period.

Southworth (1977) reports the rate of microbial degradation of anthracene to be 0.0612 hr^{-1} with a corresponding half-life of 11.3 hours, in water collected, with its attendant microbial population, from a small stream that was known to be chronically affected by industrial effluents containing anthracene. Southworth (1977) summarized his findings by stating that the persistence of anthracene in natural waters under summer conditions of temperature and illumination appears to be primarily determined by the fate processes of photolysis and degradation by microorganisms suspended in the water column. Furthermore, he reports that in large, deep (5 m), slow moving rivers, such as the upper Ohio, depth and turbidity would act to reduce the importance of photolysis, making microbial activity the major fate process. The applicability of his conclusion to fluoranthene or other structurally similar compounds is unknown at this time.

Evans *et al*. (1965) reports that phenanthrene is metabolized by soil *Pseudomonads* to 1,2-dihydroxynaphthalene via several steps involving hydroxylated intermediates. Data presented by Fedoseeva *et al*. (1968), Lorbacher *et al*. (1971), Shabad (1968), and others demonstrate that soil microbes are capable of degrading certain polycyclic aromatic hydrocarbons, primarily 3,4-benzo-pyrene, anthracene, and phenanthrene, and that the rate and degree of degradation is greatest when the soil and its microbial population have acclimated to the polycyclic aromatic hydrocarbon. Soil systems are known to provide much better conditions for biodegradation than aquatic systems. Poglazova *et al*. (1972) report that indigenous bacteria of power plant and coke oven wastewater effluents contaminated with 3,4-benzopyrene metabolized less than 15 percent of the compound.

The data presented herein seems to point in the direction of biodegradation as an important fate process for polycyclic aromatic hydrocarbons with 4 or less aromatic rings. Biodegradation is probably slower in the aquatic system than in the soil, and it may be much more important in those aquatic systems which are chronically affected by polycyclic aromatic hydrocarbon contamination.

96.4.8 Microcosm Studies, Field Studies, and Modelling

Lee et al. (1978) took crude oil enriched with a number of polycyclic aromatic hydrocarbons, including anthracene and fluoranthene, and added it as a dispersion to a controlled ecosystem enclosure suspended in Saanich Inlet, Canada. Concentrations of various aromatics were determined in water, zooplankton, oysters, and bottom sediments. Their results indicate that aromatic hydrocarbons have short residence times (on the order of a few days) in marine waters. Most, including anthracene (18 μg/l, day 1) and fluoranthene (6.2 μg/l, day 1), decreased exponentially with time during the 17 days of the experiment. For lower molecular weight polycyclic aromatics, such as benzenes, naphthalenes, anthracenes, and phenanthrenes, Lee et al. (1978) states that, " microbial degradation and evaporation (volatilization) are the primary removal processes. The concentration of higher weight aromatics, such as chrysenes, benzanthracenes, and benzpyrenes, are primarily affected by sediments and photochemical oxidation." Due to their low solubility in water, the heavier aromatics are associated with suspended particulates and after sedimentation interactions between benthic organism and bacteria. As a result, sediment becomes an important factor in their removal.

96.5 Data Summary

A summary of the data discussed above is presented in Tables 96-1.1 through 96-1.3. The summary statements presented in the tables are, for the most part, taken from fate data which apply to polycyclic aromatic hydrocarbons in general.

Table 96-1.1

Summary of Aquatic Fate of Anthracene

Environmental Process[a]	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Dissolved portion may undergo rapid photolysis.	-	~35 minutes	Medium
Oxidation	Oxidation of anthracene by RO_2 radical is slow; not a significant process.	50 liter $mol^{-1} sec^{-1}$	1600 days	Medium
Hydrolysis	Anthracene does not contain groups amenable to hydrolysis.	0	-	Medium
Volatilization	May be competitive with adsorption.	0.002 to 0.179^{-1}	18-300 hours	Low
Sorption[b]	Measured adsorption coefficients for anthracene and suspended solids are high; movement via sediment is considered to be an important transport process.	-	-	Medium
Bioaccumulation	A short-term process; anthracene is readily metabolized and long-term partitioning into biota is not a significant fate process.	-	-	Medium
Biotransformation/ Biodegradation	Anthracene can be degraded by microbes and is readily metabolized by multicellular organisms; biodegradation is probably the ultimate fate process.	< 0.0612 hr^{-1}	> 11.3 hours	Medium

---

a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. Because the solubility of this compound is relatively high, 50 percent or more may exist in true solution under conditions of normal sediment loading. Southworth (1979).

Table 96-1.2

Summary of Aquatic Fate of Fluoranthene

Environmental Process[a]	Summary Statement[b]	Rate	Half-Life ($t_{1/2}$)	Confidence of Data[c]
Photolysis	Dissolved portion may undergo rapid photolysis.	-	-	
Oxidation	Oxidation of PAH by RO_2 radical is a slow process; not a significant process.	-	-	
Hydrolysis	PAHs do not contain groups amenable to hydrolysis.	-	-	
Volatilization	Is probably not as important as adsorption as a transport process.	-	-	
Sorption	Measured adsorption coefficients for PAH and suspended solids are high; movement via sediment is considered to be an important transport process.	-	-	
Bioaccumulation	A short-term process; PAHs with 4 or less aromatic rings are readily metabolized and long-term partitioning into biota is not a significant fate process.	-	-	
Biotransformation/ Biodegradation	PAHs with 4 or less aromatic rings are degraded by microbes and are metabolized by multi-cellular organisms; biodegradation is probably the ultimate fate process.	2.2×10^{-3} µmol hr^{-1} mg^{-1} bacterial protein[d]	-	

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. Very little environmental fate data specific to fluoranthene were found; the summary statement is made from data reviewed for PAHs as a group.

c. Data on fluoranthene are not sufficient to permit confidence ranking. The confidence of the data reviewed for PAHs in general ranges from low to high.

d. Barnsley (1975).

Table 96-1.3

Summary of Aquatic Fate of Phenanthrene

Environmental Process[a]	Summary Statement[b]	Rate	Half-Life ($t_{1/2}$)	Confidence of Data[c]
Photolysis	Dissolved portion may undergo rapid photolysis.	-	-	-
Oxidation	Oxidation of PAH by RO_2 radical is slow; not a significant process.	0.01 $l \cdot mol^{-1} sec^{-1}$	8 x 10^6 days	Medium
Hydrolysis	PAHs do not contain groups amenable to hydrolysis.	-	-	-
Volatilization	Is probably not as important as adsorption as a transport process.	-	-	-
Sorption	Measured adsorption coefficients for PAH and suspended solids are high; movement via sediment is considered to be an important transport process.	-	-	-
Bioaccumulation	A short-term process; PAHs with 4 or less aromatic rings are readily metabolized and long-term partitioning into biota is not a significant fate process.	-	-	-
Biotransformation/ Biodegradation	PAHs with 4 or less aromatic rings are degraded by microbes and are readily metabolized by multicellular organisms; biodegradation is probably the ultimate fate process.	-	-	-

---

a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. Very little environmental fate data specific to phenanthrene were found; the summary statement is made from data reviewed for PAHs as a group.

c. Data on phenanthrene are not sufficient to permit confidence ranking in most cases. The confidence of the data reviewed for PAHs in general ranges from low to high.

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97. POLYCYCLIC AROMATIC HYDROCARBONS: BENZO[a]ANTHRACENE, BENZO[b]FLUORANTHENE, BENZO[k]FLUORANTHENE, CHRYSENE, PYRENE

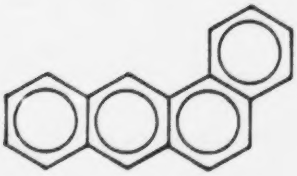
97.1 Statement of Probable Fate

The aquatic fates of five polycyclic aromatic hydrocarbons each compound containing four aromatic rings are summarized in this chapter. With the exception of benzo[a]anthracene, very little data specific to these compounds were found. Benzo[a]anthracene, however, has been relatively well studied; and in particular, an excellent study conducted by Smith et al. (1978) has been used extensively in this report. The results of the data summary suggest that these compounds will accumulate in the sediment and biota due to their tendency to adsorb strongly onto suspended particulates. Transport, therefore, is largely determined by the hydrogeologic conditions of the aquatic system. A small amount of the polycyclic aromatic hydrocarbons will be dissolved and probably will be degraded by photolysis and, to a lesser degree, by oxidation. The ultimate fate of these compounds is believed to be biodegradation and biotransformation by benthic organisms, including microbes.

97.2 Identification

Polycyclic aromatic hydrocarbons are present in the environment from both natural and anthropogenic sources. As a group, they are widely distributed in the environment, having been detected in animal and plant tissue, sediments, soils, air and surface water (Radding et al. 1976). Shackelford and Keith (1976) report that benzo[a]anthracene has been detected in industrial effluents and ambient river water; benzo[k]fluoranthene in finished drinking water, ground water, industrial effluents and ambient water; benz[b]fluoranthene and pyrene in finished drinking water, industrial effluents and ambient river water; and chrysene in ambient river water.

The chemical structures of the polycyclic aromatic hydrocarbons discussed in this section are shown below.

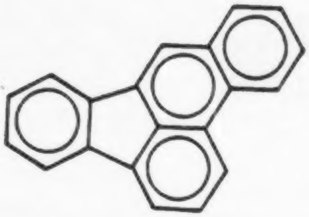


Benzo[a]anthracene

CAS NO. 56-55-3
TSL NO. CV 92750

Alternate Names

1,2-Benzanthracene
Benzo[a]anthracene
Tetraphene
Napthanthracene
2,3-Benzophenanthrene

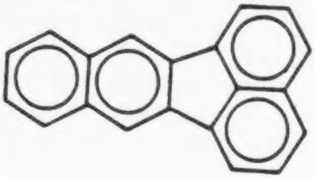


Benzo[b]fluoranthene

CAS NO. 205-99-2
TSL NO. CU 14000

Alternate Names

2,3-benzofluoranthene
Benz[e]acephenanthrylene
3,4-benzofluoranthene
B[b]F

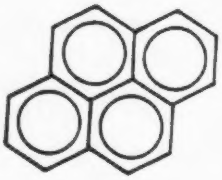


Benzo[k]fluoranthene

CAS NO. 207-08-9
TSL NO. DF 63500

Alternate Names

11,12-Benzofluoranthene
B[k]F

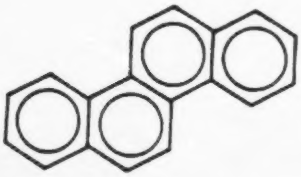


Pyrene

CAS NO. 129-00-0
TSL NO. UR 24500

Alternate Names

Benzo[def]phenanthrene



Chrysene

CAS NO. 218-01-9
TSL NO. GC 07000

Alternate Names

1,2-Benzophenanthrene
Benz[a]phenanthrene
1,2,5,6-Dibenzonaphthalene

97.3 Physical Properties

The physical properties of polycyclic aromatic hydrocarbons containing 4 aromatic rings are shown below.

	Benzo[a] Anthracene	Benzo[b] Fluoranthene	Benzo[k] Fluoranthene	Chrysene	Pyrene
Molecular Weight	228.28^{a}	252.32^{d}	252.32^{g}	228.28^{c}	202^{g}
Melting Point	$155\text{-}157^{\circ}C^{a}$	$167\text{-}168^{\circ}C^{d}$	$217^{\circ}C^{g}$	$256^{\circ}C^{c}$	$150^{\circ}C^{h}$
Vapor Pressure (20°C)	5×10^{-9} torr^{a}	$10^{-11}\text{-}10^{-6}$ torr^{e}	9.59×10^{-11} torr^{c}	$10^{-11}\text{-}10^{-6}$ torr^{e}	6.85×10^{-7} torr^{c}
Solubility in water (25°C)	0.014 mg/l^{b} .009 mg/l^{i}	NA	NA	0.002 mg/l^{b} 0.002 mg/l^{i}	0.14 mg/l^{b} 0.132 mg/l^{i}
Log Octanol/Water Partition Coefficient	5.61^{c}	6.57^{f}	6.84^{f}	5.61^{c}	5.32^{f}

(a) Smith *et al.* (1978)
(b) Mackay and Shiu (1977)
(c) Radding *et al.* (1976)
(d) IARC (1973)
(e) Estimated based on data for structurally similar compounds.
(f) Calculated as per Leo *et al.* (1971)
(g) Weast (1977)
(h) Cleland and Kingsbury (1977)
(i) May and Wasik (1978)

NA = No data found.

97.4 Summary of Fate Data

97.4.1 Photolysis

Most polycyclic aromatic hydrocarbons absorb solar radiation strongly at wavelengths above the solar cutoff (~300 nm) and may, therefore, undergo direct photolysis or photooxidation (Radding *et al*. 1976). With the exception of benzo[a]anthracene, no literature was found specifically dealing with the direct photolysis of the compounds described in this chapter. The review by Radding *et al*. (1976), however, indicates that direct photolysis in the aqueous environment may be an important fate process for these compounds. Several authors studying the photolysis of polycyclic aromatic hydrocarbons have stated that singlet oxygen is the oxidant and that the reaction products are quinones (NAS 1972; Stevens and Algar 1968).

Smith *et al*. (1978) report that the photolysis of dissolved benzo[a]anthracene is rapid in the solar wave length region, with resulting half-lives of several hours. The half-life for direct photolysis of benzo[a]anthracene in sunlight as a function of the time of day was calculated by the procedure of Zepp and Cline (1977) using a quantum yield of 3.3 x 10^{-3} and the measured UV spectrum of benzo[a]anthracene; these data for both summer and winter seasons are shown in Figure 97-1. A calculated half-life of 1 to 2 hours for midday photolysis is close to the 3-hour half-life measured by Smith *et al*. (1978) for a cloudy midday in early March.

McGinnes and Snoeyink (1974) report the direct photolysis of benzo[a]anthracene and indicate a half-life in sunlight of less than a day. Both studies (McGinnes and Snoeyink (1974), Smith *et al*. (1978)), identified one benzo[a]anthracene photo-product as a benzo[a]anthracene-7, 12-quinone; McGinnes and Snoeyink (1974) also found a second major photolysis product but were only able to identify it as a complex organic acid.

Southworth (1977) observed that anthracene dissolved in distilled water was rapidly degraded when exposed to natural sunlight, with a photolytic half-life of about 35 minutes under midday sunlight (midsummer, 35°N latitude). Using the Zepp and Cline (1977) procedure, Southworth (1977) predicts that, in shallow waters, anthracene will exhibit a photolytic half-life of 4.8 hours under average winter solar conditions at 35°N latitude.

Whether the remaining polycyclic aromatic hydrocarbons undergo photolysis with half-lives similar to those reported above is not clear from the literature reviewed. The selection of direct photolysis as a significant fate process is, therefore, only speculative at this time.

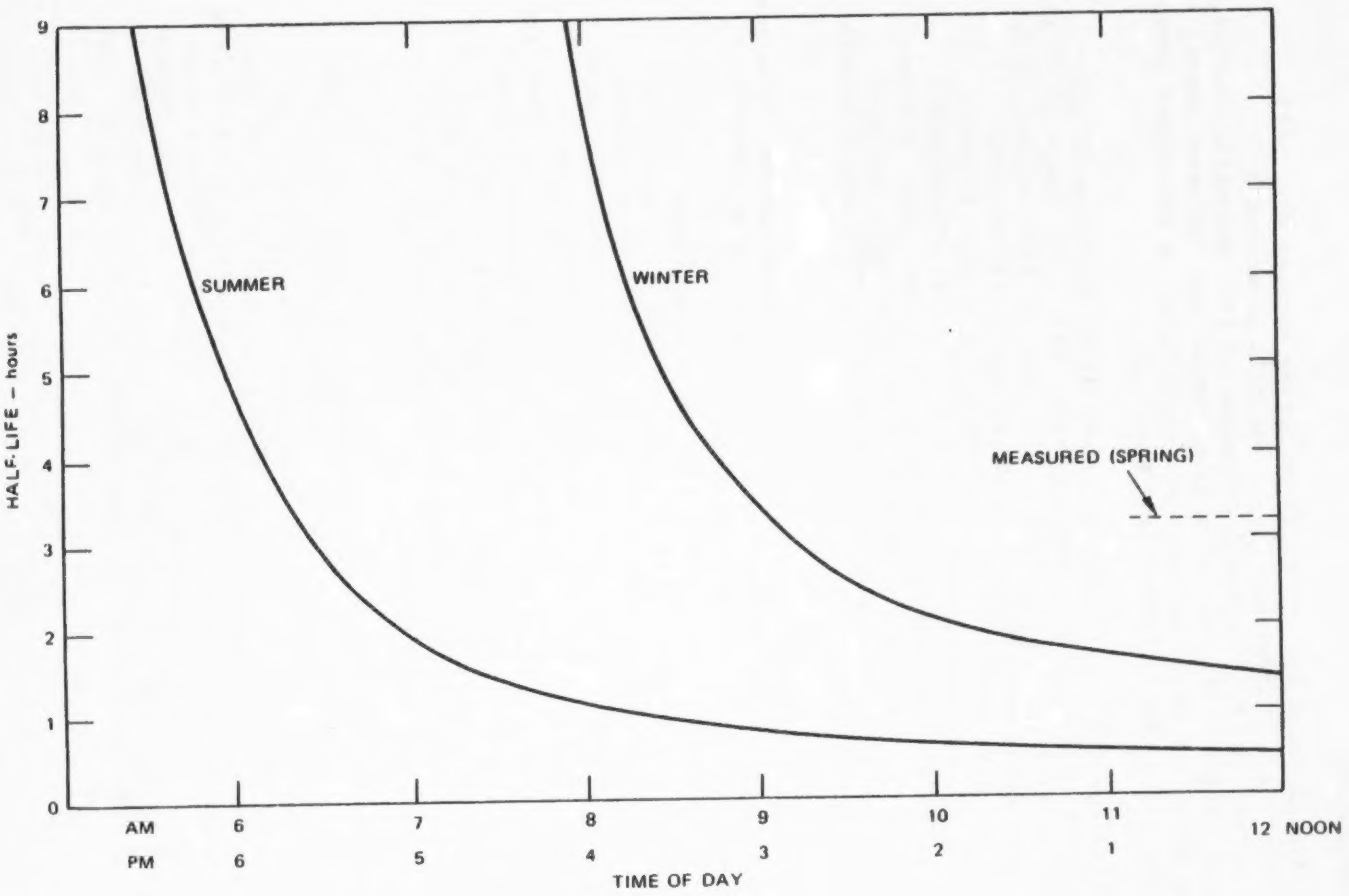


Figure 97-1 Seasonal and daily variation of the photolytic half-life of benzo[a]anthracene using the Zepp and Cline (1977) model. Data measured by Smith _et_ _al_. (1978).

97.4.2 Oxidation

In natural water the principal oxidizing species are: (1) alkylperoxy ($RO_2\cdot$) and hydroperoxy ($HO_2\cdot$) radicals generated by photolytic cleavage of trace carbonyl compounds or from enzymatic sources, and (2) singlet oxygen. The role of singlet oxygen was discussed above; it is considered to be the major oxidant species involved in the direct photolysis of polycyclic aromatic hydrocarbon molecules.

Several qualitative studies of free-radical oxidation of polycyclic aromatic hydrocarbons have been reported (NAS 1972; Tipson 1965) and are summarized by Radding et al. (1976). The rates of free radical oxidation by $RO_2\cdot$ vary among specific polycyclic aromatic hydrocarbons (Mahoney 1965) and also depend on the concentration of $RO_2\cdot$ radicals, which Radding et al. (1976) estimate to be a 10^{-10} molar steady-state concentration under average daily illumination in natural water systems. Half-lives for the reaction of $RO_2\cdot$ radical with anthracene, benzo[a]-pyrene, and perylene have been calculated to be 1600, 9900, and 1600 days, respectively (Radding et al. 1976).

The susceptibility of benzo[a]anthracene to free radical oxidation was examined by Smith et al. (1978). From their experimental laboratory conditions, they obtained a pseudo-first order rate constant (k_{ox}-($RO_2\cdot$)) of 1.53×10^{-4} sec^{-1} for oxidation of benzo[a]anthracene with the $RO_2\cdot$ radical. This rate corresponds to a half-life of 1.3 hours. By extrapolating these laboratory conditions to environmental conditions where the temperature is 25°C and the concentration of $RO_2\cdot$ radical is 10^{-10} M, the half-life of benzo[a]anthracene toward oxidation is estimated to be about 38 hours (Smith et al. 1978). Thus, the free-radical oxidation of benzo[a]anthracene in the environment is rapid and may be competitive with photolysis as a chemical fate process. It appears probable, however, that the half-life for oxidation by the $RO_2\cdot$ radical is longer for most other polycyclic aromatics and that faster processes determine their aquatic fate.

Chlorine and ozone, when used to disinfect drinking water, are strong oxidants which can chemically react with any polycyclic aromatic hydrocarbon present in the water to form quinones. Perry and Harrison (1977) studied the removal by chlorination of 8 polycyclic aromatic hydrocarbons including benzo[a]anthracene, benzo[k]fluoranthene, and pyrene from waters. Concentrations ranged from 30-860 ng/l, amounts normally encountered in raw waters. With 2.2 mg/l free chlorine, pH 6.8 and 20°C, benzo-[a]anthracene and pyrene were 50% degraded after 20 minute contact time while only 20% of benzo[k]fluoranthene was degraded after 20 minutes. Decreased pH and increased temperature both increased the rate of degradation. Data summarized by Radding _et al_. (1976) indicate that benzo[a]pyrene will have an initial ten-minute half-life when exposed to a 0.5 mg/1 solution of chlorine in water (Trakhtman and Manita 1966). From observations of Il'nitskii _et al_. (1968), Radding _et al_. (1976) calculated half-lives of pyrene, benzo[a]pyrene, and benzo[a]anthracene with ozone in water to be as short as one minute. Pyrene is estimated to have a half-life of 41 mimutes in the presence of ozone at a concentration of 10^{-4} M (Radding, _et al_. (1976)) While these data are not specific to other polycyclic aromatic hydrocarbons, oxidation by chlorine and ozone may be a significant fate process when these oxidants are available in sufficient quantity.

97.4.3 Hydrolysis

Polycyclic aromatic hydrocarbons do not contain groups amenable to hydrolysis. Hydrolysis, therefore, is not thought to be a significant fate process for benzo[a]anthracene (Smith _et al_. 1978) or for the other compounds in this group.

97.4.4 Volatilization

To assess the importance of volatilization as a transport process for polycyclic aromatic hydrocarbon in natural water, a volatilization rate is necessary. Several authors have suggested ways to estimate volatilization rates of compounds from water using theoretical considerations (Mackay and Wolkoff 1973; Mackay and Leinonen 1975). These methods, however, contain sufficient practical deficiences which make them difficult to use in estimating the volatilization from natural waters.

Smith _et al_. (1978) measured the volatilization rate of benzo[a]pyrene and benzo[a]anthracene using the theory derived by Tsivoglou (1967) and described by Hill _et al_. (1976). The volatilization half-lives of benzo[a]pyrene and benzo[a]anthracene in a rapidly-stirred aqueous solution were 22 and 89 hours, respectively. These half-lives are relatively long when compared to those related to direct photolysis. Smith _et al_. (1978) further state that when benzo[a]pyrene and benzo[a]anthracene are sorbed onto sediments, volatilization of the sorbed compound is presumed to be very slow.

In a laboratory study of a model stream 1.0 m in depth, Southworth (1979) measured the volatilization rates of several polycyclic aromatic hydrocarbons containing from 2 to 5 rings. He found for example that the volatilization rate in general decreases as the vapor pressure decreases both of which are inversely related to the number of aromatic rings, and that the volatilization rate is highly dependent upon the mixing rates within both the water and associated air columns. Polycyclic aromatics containing fewer aromatic rings such as naphthalene and anthracene are also more sensitive to mixing within the water column than those containing a greater number of aromatic rings such as benzo[a]pyrene and benzo[a]anthracene. For example, the volatilization half-life for naphthalene increased 7.5 times compared to 1.4 for benzo[a]pyrene following a 10 fold increase in stream flow velocity. The volatilization rate was less sensitive to changes in wind velocity but still increased up to 5 times for a 10 fold increase in velocity and the half-times for volatilization of naphthalene, anthracene, benzo[a]anthracene and benzo[a]pyrene with maximum wind velocity (4 m/sec) and stream current velocity (1 m/sec) were 3.2, 16, 150 and 430 hours respectively. Since these values represent the theoretically expected maximum (not taking into account physical factors which slow evaporation such as sorption) Southworth (1979) concludes that the rate of vaporization of polycyclic aromatics with 4 or more rings will be insignificant under all conditions and the evaporation of lower molecular weight compounds such as naphthalene may be substantial only in a clear, rapidly flowing stream.

Volatilization of some high molecular weight, sparingly soluble organics has been shown to be surprisingly rapid owing to exceptionally high activity coefficients (Mackay and Leinonen 1975). Polycyclic aromatic hydrocarbons may have similarly high activity coefficients; based on available information, however, volatization does not appear to be an important transport process for polycyclic aromatic hydrocarbons in general.

97.4.5 Sorption

With the exception of benzo[a]anthracene, the data reviewed did not reveal specific partition coefficients between water and suspended particulate matter or biota for the polycyclic aromatic hydrocarbon discussed in this chapter. In general, polycyclic aromatic hydrocarbons are widely distributed in the environment and are transported suspended onto particulate matter in air or water (NAS 1972, Radding *et al*. 1976). The calculated octanol/water partition coefficients, which all exceed 5.32 (Leo *et al*. 1971, Radding 1976), indicate that these compounds should be strongly adsorbed onto suspended particulate matter, especially particulates high in organic content.

The data collected by Smith *et al*. (1978) and others indicate that most polycyclic aromatic hydrocarbons, and specifically benzo[a]anthracene and benzo[a]pyrene, will accumulate in the sediment and biota portions of the aquatic environment and that adsorption is the dominant transport process for them. Figure 97-2 illustrates the effect of suspended solids on benzo[a]anthracene when discharged to a hypothetical partially mixed river system. These authors report partition coefficients (Kp) of 150,000 for benzo[a]pyrene and 21,000 for benzo[a]anthracene between water and sediment

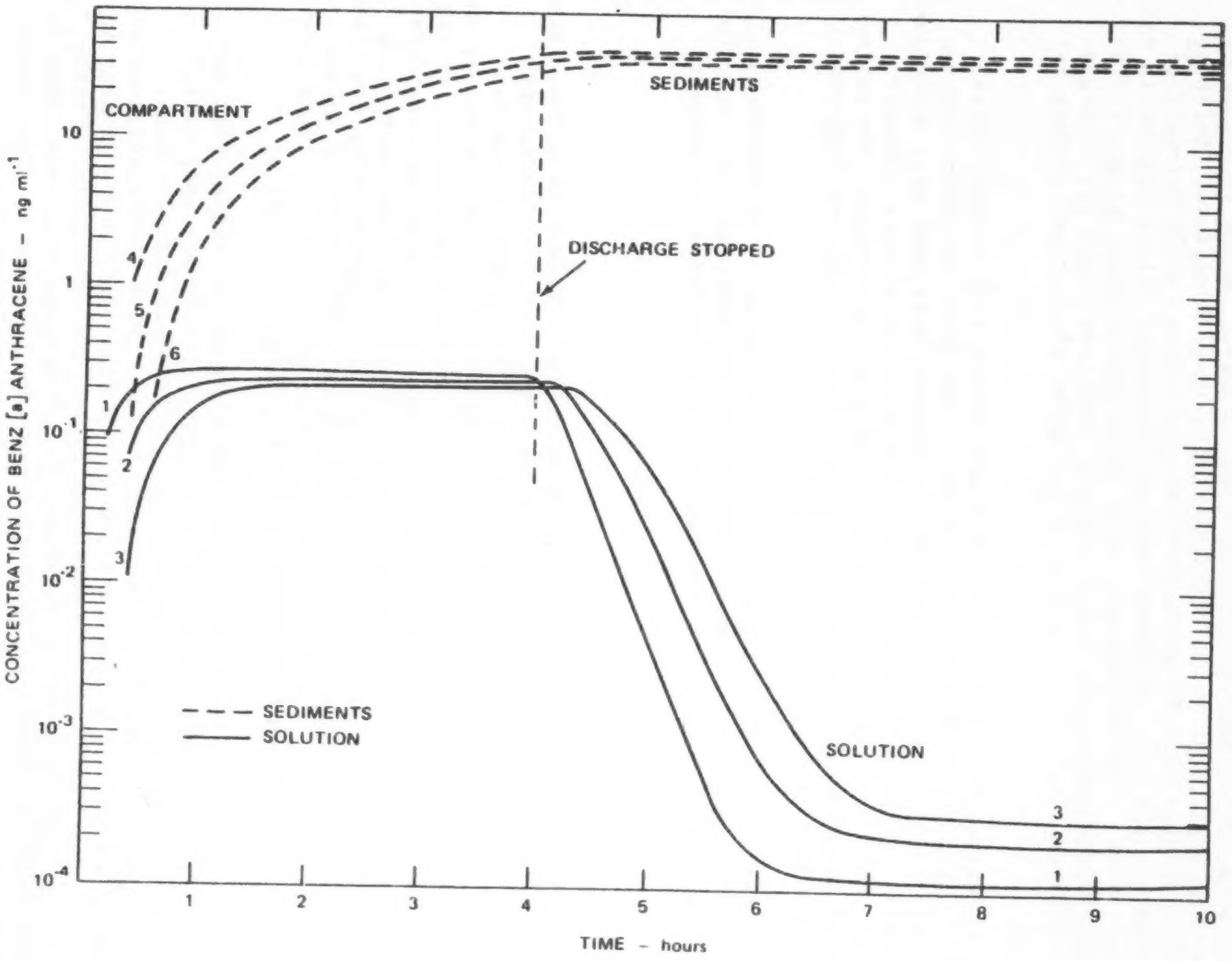


Figure 97-2 Effect of suspended solids on benzo[a]anthracene in a partially mixed, hypothetical river system. Taken from Smith et al. (1978).

containing 5 percent organic carbon, and indicate that sorption onto sediments is strongly correlated with the organic carbon levels in sediments. Using a one-compartment model which simulates river conditions, Smith et al. (1978) predict that 83 percent of benzo[a]pyrene and 71 per-cent of benzo[a]anthracene will be sorbed onto the suspended solids present in the simulated river. The experimental work performed by Smith et al. (1978) with benzo[a]anthracene and benzo[a]pyrene shows that both are strongly sorbed onto bacterial cells as well as suspended abiotic particulate matter.

Southworth (1977) showed that anthracene (log octanol/water partition coefficient of 4.45) was sorbed by inorganic sediments and suspended organic particulates. The organic particulates used were autoclaved yeast cells. A partition coefficient (solids/water) of approximately 25,000 was observed, which is, indicative of a strong tendency for anthracene to be biosorbed. Sorption by inorganic particulates was less and resulted in a partition coefficient of 1600.

These data indicate that the polycyclic aromatic hydrocarbons discussed in this chapter, will accumulate in the sediment and biota portions of the aquatic environment and that adsorption is probably the dominant aquatic transport process.

97.4.6 Bioaccumulation

A large number of polycyclic aromatic hydrocarbons have been identified in living matter, and data collected from field and laboratory studies indicate that organisms throughout the phylogenetic scale can incorporate and metabolize them (Radding et al. 1976). With the exception of benzo[a]anthracene, specific data on bioaccumulation of polycyclics discussed in this chapter were not found; conclusions are based on consideration of their properties as a group. A relatively high (calculated) log octanol/water partition coefficients (log P >5.31), together with the theoretical and empirical indications that compounds with high log P values tend to accumulate in biota (Neely et al. 1974), indicate that these polycyclic aromatic hydrocarbons probably would be bioaccumulated.

The sorption of benzo[a]pyrene and benzo[a]anthracene onto bacterial cells was found to be rapid with a partition coefficient (cell/-water) of approximately 10^4 (Smith et al. 1978). Niaussat and Auger (1970) report that biota in a lagoon contaminated with 3,4-benzopyrene and perylene accumulated both compounds, and that accumulation was greater in those species occupying a niche near the top of the food chain. Freshwater worms (*Tubifex sp.*), when exposed to 3,4 benzopyrene, were shown to accumulate the compound with increasing exposure followed by slow depuration when placed in uncontaminated water (Scaccini-Cicatelli 1966).

Southworth et al. (1978) determined the bioaccumulation potential of seven polycyclic aromatic hydrocarbons including naphthalene, anthracene, phenanthrene, pyrene, methylanthracene, benzo[a]anthracene and perylene in Daphnia pulex. All were rapidly taken up with naphthalene and anthracene reaching an equilibrium within 2 and 6 hours respectively and benzo[a]anthracene in 24 hours. The equilibrium concentration factors increased dramatically with increasing molecular weight ranging from 100 for naphthalene to 10,000 for benzo[a]anthracene. The calculated n-octanol/-water partition coefficients were found to be a good predictor of bioaccumulation potential in Daphnia. The rapid bioaccumulation suggests that body burden in zooplankton will follow closely the aqueous concentration of polycyclic aromatics and not be dependent upon food chain.

Using radiolabeled naphthalene, Lee et al. (1972) determined that, for various marine invertebrates, naphthalene is accumulated in tissue, within hours of exposure, and stored in the liver where it is rapidly metabolized. Naphthalene and its metabolites are then transferred to the bile and eventually excreted.

Wagner and Siddiqi (1971) report that the increased concentration of benzo[b]fluoranthene in the soil caused an increase in its concentration in summer wheat and rye growing on the soil.

The data discussed above support the premise that, although polycyclic aromatic hydrocarbons are rapidly bioaccumulated, those that contain 4 or less aromatic rings may also be rapidly metabolized and eliminated (excreted) from the organism. Bioaccumulation, therefore, is considered to be short-term, and is probably unlike the long-term bioaccumulation that has been demonstrated for some of the more persistent chlorinated organics (e.g., PCB's, DDT).

If the bioaccumulation of polycyclic aromatic hydrocarbons is short-term, the compound should be available for in vivo metabolism. One important aspect of the data reviewed is that accumulation into biota does not provide for significant long-term environmental storage; thus, bioaccumulation is not considered an important fate process.

97.4.7 Biotransformation and Biodegradation

The degradation and metabolism of polycyclic aromatic hydrocarbons and the identification of their metabolites are known from studies conducted with bacteria and mammals, as summarized by the National Academy of Sciences (1972) and Radding et al. (1976). In mammals, the major metabolites of these compounds are hydroxylated derivatives and epoxides (Sims 1970); degradation by mammals, however, is considered incomplete with the parent compound and the metabolites being excreted via the urinary system (Evans et al. 1965).

Bacteria have been shown to utilize some polycyclic aromatic hydrocarbon compounds as a sole carbon source for growth, and evidence summarized by Radding et al. (1976) suggest that bacteria can degrade these compounds much more completely than mammals. Evidence for bacterial degradation comes from studies conducted on only a few polycyclic aromatic hydrocarbons.

The microbial degradation of polycyclic aromatic hydrocarbons was studied by Groenewegen and Stolp (1975). Their data show that tricyclic aromatic hydrocarbons are capable of being degraded by microbes but report that such degradation is not known for higher polycyclic hydrocarbons. They further report that organic compounds which are difficult to degrade are sometimes co-oxidized by microbes although these organisms cannot use them as their sole source of carbons. Using a mixed "cocktail" of polycyclic aromatic hydrocarbons, Groenewegen and Stolp (1975) found that phenanthrene, pyrene, 1,2-benzanthracene, and 3,4-benzopyrene were degraded significantly. Fluorene and fluoranthene were only somewhat degraded and chrysene was not degraded to any measurable degree.

Herbes and Schwall (1978) found that naphthalene (half-time 5 hours) and anthracene (half-time 280 hours) are degraded rapidly in hydrocarbon contaminated sediment samples. The half-times for polycyclic aromatic hydrocarbons containing 4 or more rings, however, were much longer (benzo[a]anthracene, 7,000 hours and benzo[a]pyrene, 21,000 hours) causing these authors to suggest that such compounds may persist even in sediments that have received chronic polycyclic aromatic hydrocarbon inputs. In addition, half-life times in samples obtained from uncontaminated streams were 10 to 400 times longer than those from contaminated streams.

Evans et al. (1965) reports that phenanthrene is metabolized by soil Pseudomonads to 1,2-dihydroxynaphthalene via several steps involving hydroxylated intermediates. Data presented by Fedoseeva et al. (1968), Lorbacher et al. (1971), Shabad (1968), and others demonstrate that soil microbes are capable of degrading certain polycyclic hydrocarbons, primarily 3,4-benzopyrene, anthracene, and phenanthrene, and that the rate and degree of degradation are greatest when the soil and its microbial population have acclimated to the compound. Soil systems are known to provide much better conditions for biodegradation than aquatic systems. Poglazova et al. (1972) report that indigenous bacteria of power plant and coke oven wastewater effluents contaminated with 3,4-benzopyrene metabolized less than 15 percent of the compound.

Data presented by Smith et al. (1978) seem to indicate that long-term exposure of microbes is necessary before a bacterial population is capable of degrading polycyclic aromatic hydrocarbons. Their work with three sets of experimental conditions used in attempting to develop enrichment cultures to degrade benzo[a]pyrene and benzo[a]anthracene failed to yield systems capable of significant biodegradation. Smith et al. (1978) surmise that there is a natural preselection and induction process that occurs under natural conditions and that their experimental conditions did not allow for the proper induction period.

Southworth (1977) reports the rate of microbial degradation of anthracene to be 0.0612 hr^{-1} with a corresponding half-life of 11.3 hours. His work differs from Smith et al. (1978) in that he collected water, with its attendant microbial population, from a small stream that was known to be chronically affected by industrial effluents containing anthracene. Southworth (1977) summarized his findings by stating that the persistence of anthracene in natural waters under summer conditions of temperature and illumination appears to be primarily determined by the fate processes of photolysis and degradation by microorganisms suspended in the water column. Furthermore, he reports that in large, deep (5 m), slow moving rivers, such as the upper Ohio, depth and turbidity would act to reduce the importance of photolysis, making microbial activity the major fate process.

Gibson et al. (1975), using enrichment techniques with biphenyl as a sole carbon source, isolated a bacterium with a subsequent mutant strain that converted benzo[a]anthracene to four dihydrodiols. These were further oxidized by the parent bacterial strain into some unidentified organic acids. Gibson's work indicates the possible value of using chemically related products for development of enrichment cultures and the utility of this procedure in degradation studies with more complex products.

The data presented herein appears to indicate that biodegradation can be an important fate process for polycyclic aromatic hydrocarbons in general. Biodegradation is probably slower in the aquatic system than in the soil, and biodegradation may be much more important in those aquatic systems which are chronically affected by polycyclic aromatic contamination. The bi- and tricyclic species may be more biodegradable than those containing a large number of aromatic rings.

97.5 Data Summary

The results of the data review indicates that polycyclic aromatic hydrocarbons will accumulate in the sediment and biota and will be transported with the suspended sediment. Some amount will be dissolved in water and will probably be degraded by direct photolysis. The ultimate fate of the adsorbed compounds is believed to be biodegradation and transformation by benthic organisms, microbes, and vertebrate organisms in the food chain.

The half-lives of dissolved benzo[a]anthracene, calculated for individual fate and transport processes following a spill, are shown in Table 97-1 as developed by Smith *et al*. (1978). Although the half-lives vary among types of aquatic systems, sorption dominates as a primary transport process. The role of biodegradation and transformation is not well represented since Smith *et al*. (1978) were not able to develop degrading cultures.

A summary of the data discussed above is presented in Tables 97-2.1 through 97-2.5. Very little data specific to other polycyclic aromatic hydrocarbons containing 4 aromatic rings were found, and rates or half-lives for these are not presented in the table. The summary statements presented in the tables are, for the most part, derived from fate data which apply to polycyclic aromatic hydrocarbons in general.

Table 97-1. Transport and Fate of Benzo[a]anthracene
Predicted by a One-Compartment Model
(Smith *et al*. 1978)

Process	Stream	Eutrophic Pond	Eutrophic Lake	Oligotrophic Lake
Photolysis, $t_{1/2}$ in hrs.	20	50	50	10
Oxidation, $t_{1/2}$ in hrs.[1]	38	38	38	38
Volatilization, $t_{1/2}$ in hrs.	>1000	>1000	>1000	>1000
Hydrolysis, $t_{1/2}$ in hrs.	Large	Large	Large	Large
Biodegradation, $t_{1/2}$ in hrs.	Large	Large	Large	Large
$t_{1/2}$ for all processes (except dilution) in hrs.	13	22	22	8
$t_{1/2}$ for all processes (including dilution) in hrs.	0.55	22	22	8
Amount of sorbed compound (mg M^{-3})	2.5	7.5	1.25	1.25
Percentage sorbed	71%	88%	55%	55%

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[1] Based on a peroxy radical concentration of 10^{-10} M

Table 97-2.1

Summary of Aquatic Fate of Benzo[a]anthracene

Environmental Process[a]	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Dissolved portion may undergo rapid photolysis.	$\sim 6 \times 10^{-5}$ sec^{-1}	10-50 hrs	Medium
Oxidation	Oxidation of PAH by RO_2 radicals is slow; not a significant process.	5×10^{3} m^{-1}sec^{-1}	38 hrs	Medium
Hydrolysis	PAHs do not contain groups amenable to hydrolysis.	0	-	High
Volatilization	Is probably not as important as adsorption as a transport process.	8×10^{3} hr^{-1}	~90 hrs	Medium
Sorption	Measured adsorption coefficients for PAH and suspended solids are high; movement in sediment is considered an important transport process.	Kp=26,200	-	Medium
Bioaccumulation	A short-term process; PAHs with 4 or less aromatic rings are readily metabolized and long-term partitioning into biota is not a significant fate process.	-	-	Low
Biotransformation/ Biodegradation	PAHs with 4 or less aromatic rings are degraded by microbes and are readily metabolized by multicellular organisms; biodegradation is probably the ultimate fate process.	-	-	Low

---

[a] There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

Table 97-2.2

Summary of Aquatic Fate of Benzo[b]fluoranthene

Environmental Process [a]	Summary Statement [b]	Rate	Half-Life ($t_{1/2}$)	Confidence of Data [c]
Photolysis	Dissolved portion may undergo rapid photolysis.			
Oxidation	Oxidation of PAH by RO_2 radical is slow; not a significant process.			
Hydrolysis	PAHs do not contain groups amenable to hydrolysis.			
Volatilization	Is probably not as improtant as adsorption as a transport process.			
Sorption	Measured adsorption coefficients for PAH and suspended solids are high; movement in sediment is considered an important transport process for PAH.			
Bioaccumulation	A short-term process; PAHs with 4 or less aromatic rings are readily metabolized and long-term partioning into biota is not a significant fate process.			
Biotransformation/ Biodegradation	PAHs with 4 or less aromatic rings are degraded by microbes and are readily metabolized by multicellular organisms; biodegradation is probably the ultimate fate process.			

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. Very little environmental fate data specific to benzo[b]fluoranthene were found; the summary statement is made from data reviewed for PAHs as a group.

c. Data on benzo[b]fluoranthene are not sufficient to permit confidence ranking. The confidence of the data reviewed for PAHs in general ranges from low to high.

Table 97-2.3

Summary of Aquatic Fate of Benzo[k]fluoranthene

Environmental Process[a]	Summary Statement[b]	Rate	Half-Life ($t_{1/2}$)	Confidence of Data[c]
Photolysis	Dissolved portion may undergo rapid photolysis.			
Oxidation	Oxidation of PAH by RO_2 radical is slow; not a significant process.			
Hydrolysis	PAHs do not contain groups amenable to hydrolysis.			
Volatilization	Is probably not as important as adsorption as a transport process.			
Sorption	Measured adsorption coefficients for PAH onto suspended solids are high; movement in suspended sediment is considered an important transport process for PAH.			
Bioaccumulation	A short-term process; PAHs with 4 or less aromatic rings are readily metabolized and long-term partitioning into biota is not a significant fate process.			
Biotransformation/ Biodegradation	PAHs with 4 or less aromatic rings are degraded by microbes and are readily metabolized by multicellular organisms; biodegradation may be the ultimate fate process.			

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[a] There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

[b] Very little environmental fate data specific to benzo[k]fluoranthene were found; the summary statement is made from data reviewed for PAHs as a group.

[c] Data on benzo[k]fluoranthene are not sufficient to permit confidence ranking. The confidence of the data reviewed for PAHs in general ranges from low to high.

Table 97-2.4

Summary of Aquatic Fate of Chrysene

Environmental Process[a]	Summary Statement[b]	Rate	Half-Life ($t_{1/2}$)	Confidence of Data[c]
Photolysis	Dissolved portion may undergo rapid photolysis.			
Oxidation	Oxidation of PAH by RO_2 radical is slow; not a significant process.			
Hydrolysis	PAHs do not contain groups amenable to hydrolysis.			
Volatilization	Is probably not as important as adsorption as a transport process.			
Sorption	Measured adsorption coefficients for PAH and suspended solids are high; movement in sediment is considered to be an important transport process.			
Bioaccumulation	A short-term process; PAHs with 4 or fewer aromatic rings are readily metabolized and long-term partitioning into biota is not a significant fate process.			
Biotransformation/ Biodegradation	PAHs with 4 or fewer aromatic rings are degraded by microbes and are readily metabolized by multicellular organisms; biodegradation is probably the ultimate fate process.			

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. Very little environmental fate data specific to chrysene were found; the summary statement is made from data reviewed for Polycyclic aromatic hydrocarbons.

c. Data on chrysene are not sufficient to permit confidence ranking. The confidence of the data reviewed for polycyclic aromatic hydrocarbons in general ranges from low to high.

Table 97-2.5

Summary of Aquatic Fate of Pyrene

Environmental Process[a]	Summary Statement[b]	Rate	Half-Life ($t_{1/2}$)	Confidence of Data[c]
Photolysis	Dissolved portion may undergo rapid photolysis.	-	-	
Oxidation	Oxidation of PAH by $RO_2^{\cdot}$ radical is slow; not a significant process.	-	1,000 days	
Hydrolysis	PAHs do not contain groups amenable to hydrolysis.	-	-	
Volatilization	Is probably not as important as adsorption as a transport process.	-	-	
Sorption	Measured adsorption coefficients for PAH and suspended solids are high; movement in suspended sediment is considered an important transport process.	-	-	
Bioaccumulation	A short-term process; PAHs with 4 or less aromatic rings are readily metabolized and long-term partitioning into biota is not a significant fate process.	-	-	
Biotransformation/ Biodegradation	PAHs with 4 or fewer aromatic rings are degraded by microbes and are readily metabolized by multicellular organisms; biodegradation is probably the ultimate fate process.	-	-	

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. Very little environmental fate data specific to pyrene were found; the summary statement is made from data reviewed for PAHs as a group.

c. Data on pyrene are not sufficient to permit confidence ranking. The confidence of the data reviewed for PAHs in general ranges from low to high.

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98. POLYCYCLIC AROMATIC HYDROCARBONS: BENZO[ghi]PERYLENE, BENZO[a]PYRENE, DIBENZO[a,h]ANTHRACENE INDENO[1,2,3-cd]PYRENE

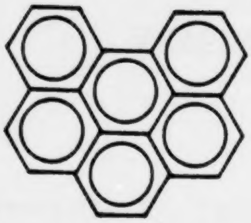
98.1 Statement of Probable Fate

Very little data specific to benzo[ghi]perylene, indeno[1,2,3-ed]pyrene and dibenzo[a,h]anthracene, were found; the aquatic fate of these compounds is inferred from data summarized for benzo[a]pyrene and polycyclic aromatic hydrocarbons in general. The results of the data summary, suggests that the aromatic compounds discussed in this chapter, each containing 5 or 6 aromatic rings, are relatively insoluble in water (0.00026 mg/l for benzo[ghi]perylene to 0.062 mg/l for indeno[1,2,3-cd]pyrene) and have relatively high log octanol/water partition coefficients. As a result, they will adsorb onto suspended particulates and biota, and their transport will be largely determined by the hydrogeologic conditions of the aquatic system. That portion dissolved in the water column will probably undergo direct photolysis at a rapid rate. The ultimate fate of these compounds and in particular benzo[a]pyrene is believed to be biodegradation and biotransformation by benthic organisms, although the processes may be very slow.

98.2 Identification

The polycyclic aromatic hydrocarbons benzo[ghi]perylene, benzo[a]pyrene, dibenzo[a,h]anthracene and indeno[1,2,3-cd]pyrene are present in the environment from both natural and anthropogenic sources. Hase and Hites (1976) doubt that true biosynthesis of polycyclic aromatic hydrocarbons has ever been observed. They state that bacteria probably do not produce polycyclic aromatic hydrocarbons but rather bioaccumulate them. As a group, polycyclic aromatic hydrocarbons are widely distributed in the environment, having been detected in animal and plant tissue, sediments, soils, air and surface water (Radding *et al*. 1976). Shackelford and Keith (1976) report that benzo[a]pyrene has been detected in industrial effluents, ambient river water, and drinking water, benzo[ghi]perylene in drinking water, ground water, industrial effluents and ambient river water, indeno[1,2,3-cd]pyrene in finished drinking water and ambient river water and dibenzo[a,h]anthracene in finished drinking water.

The chemical structure of the polycyclic aromatic hydrocarbons discussed in this section are as follows.

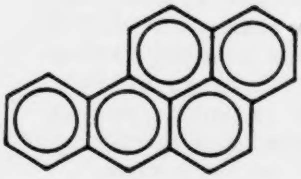


Benzo[ghi]perylene

CAS NO. 191-24-2
TSL NO. DJ 36750

Alternate Names

1,12-Benzoperylene

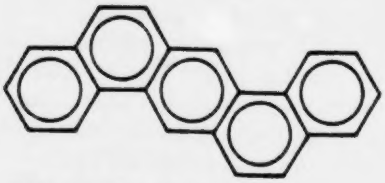


Benzo[a]pyrene

CAS NO. 50-32-8
TSL NO. DJ 36750

Alternate Names

3,4-Benzopyrene
BaP

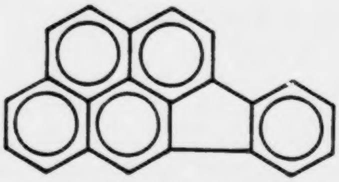


Dibenzo[a,h]anthracene

CAS NO. 53-70-3
TSL NO. HN 26250

Alternate Names

DB[a,h]A
1,2,5,6-Dibenzanthracene
DBA



Indeno[1,2,3-cd]pyrene

CAS NO. 193-39-5
TSL NO. None assigned

Alternate Names

2,3-0-Phenylenepyrene
IP

98.3 Physical Properties

The general physical properties of the polycyclic aromatic hydrocarbons having 5 or more aromatic rings which are discussed in this chapter are shown below.

	Benzo[ghi] perylene	Benzo[a] pyrene	Dibenzo[a,h] anthracene	Indeno[1,2,3-cd] pyrene
Molecular weight	276[a]	252[b]	278.36[a]	276.34[a]
Melting point	222°C[c]	179°C[b]	270°C[a]	162.5-164°C[a]
Vapor pressure (torr)	$\sim 10^{-10}$[d,h]	5×10^{-9}[b,e]	$\sim 10^{-10}$[d,h]	$\sim 10^{-10}$[d,h]
Solubility in water(25°C)	0.00026mg/l[f]	0.0038mg/l[f]	0.0005mg/l[g]	NA
Log octanol/water partition coefficient	7.23[i]	6.04[j]	5.97[i]	7.66[i]

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a) Weast 1977
b) Smith *et al*. 1978
c) Cleland and Kingsbury 1977
d) 20°C
e) 25°C
f) Mackay and Shiu 1977
g) Davis *et al*. 1942
h) Estimated, based on data for structurally similar compounds.
i) Calculated according to Leo *et al*. 1971
j) Radding *et al*. 1976
NA No data found

98.4 Summary of Fate Data

98.4.1 Photolysis

All polycyclic aromatic hydrocarbons absorb solar radiation strongly at wavelengths above the solar cutoff (~300 nm) and may, therefore, undergo direct photolysis or photooxidation (Radding *et al*. 1976). Several authors studying the photolysis of other polycyclic aromatic hydrocarbons have stated that singlet oxygen is the oxidant and that the reaction products are quinones (NAS 1972; Stevens and Algar 1968). Although no literature was found specifically dealing with the direct photolysis of benzo[ghi]perylene, dibenzo[a,h]anthracene and indeno[1,2,3-cd]pyrene, the review by Radding *et al*. 1976 indicates that direct photolysis in the aqueous environment may be an important fate process for these compounds. Smith *et al*. (1977) report that photolysis of dissolved benzo[a]pyrene is rapid in the solar spectral region with half-lives of several hours.

Smith *et al*. (1978) calculated the half-life for direct photolysis of benzo[a]pyrene in sunlight as a function of the time of day by the procedure of Zepp and Cline (1977) using a quantum yield of 8.9×10^{-4} and the measured UV spectrum of benzo(a)pyrene. The data for the summer and winter seasons are shown in Figure 98-1. The calculated half-life of 1.2 hours for midday photolysis in winter agrees closely with the measured half-lives of 1.1 and 0.7 hour. A similar treatment for benzo[a]anthracene resulted in a 2 hour half-life for that compound. The half-lives measured by Smith *et al*. (1978) are computed from a rate constant of 2.8×10^{-4} sec^{-1} in noonday sunlight in mid-December. A similar treatment for benzo[a]anthracene resulted in a 2 hour half-life for that compound. The photolysis of benzo[a]pyrene by Smith *et al*. (1978) yielded a mixture of three quinones - the 3,6-, 1,6-, and 6,12-isomers.

Southworth (1977) observed that anthracene dissolved in distilled water was rapidly degraded when exposed to natural sunlight, with a photolysis half-life of about 35 minutes under midday sunlight (midsummer, 35°N latitude). Using the Zepp and Cline (1977) procedure, Southworth (1977) predicts that, in shall waters, anthracene will exhibit a photolytic half-life of 4.8 hours under average winter solar conditions at 35°N latitude.

Smith *et al*. (1978) report that the photolysis of benzo[a]pyrene conducted in natural waters or in pure water containing humic acid showed slower photolytic rates than those experiments conducted in pure water. For example, photolysis of benzo[a]pyrene in the presence of humic acid in pure water was found to be five times slower than the photolysis in pure water, while natural water showed a somewhat smaller reduction in the rate of photolysis. The mechanism(s) that causes a reduction in the photolysis rate is not well understood. It is possible that organic or inorganic substances may quench the compound which is in the excited state or participate in complex formation that alters the ground state of the compound.

McGinnes and Snoeyink (1974) also observed inhibition of photolysis when benzo(a)pyrene was adsorbed on kaolinite clay. They surmise that products formed during photolysis inhibit the rate of photolysis. These effects may occur by several mechanisms, including competitive reactions of the associated organic material with the oxidizing agent(s) found during the photolysis of benzo[a]pyrene. Andelman of Suess (1970)

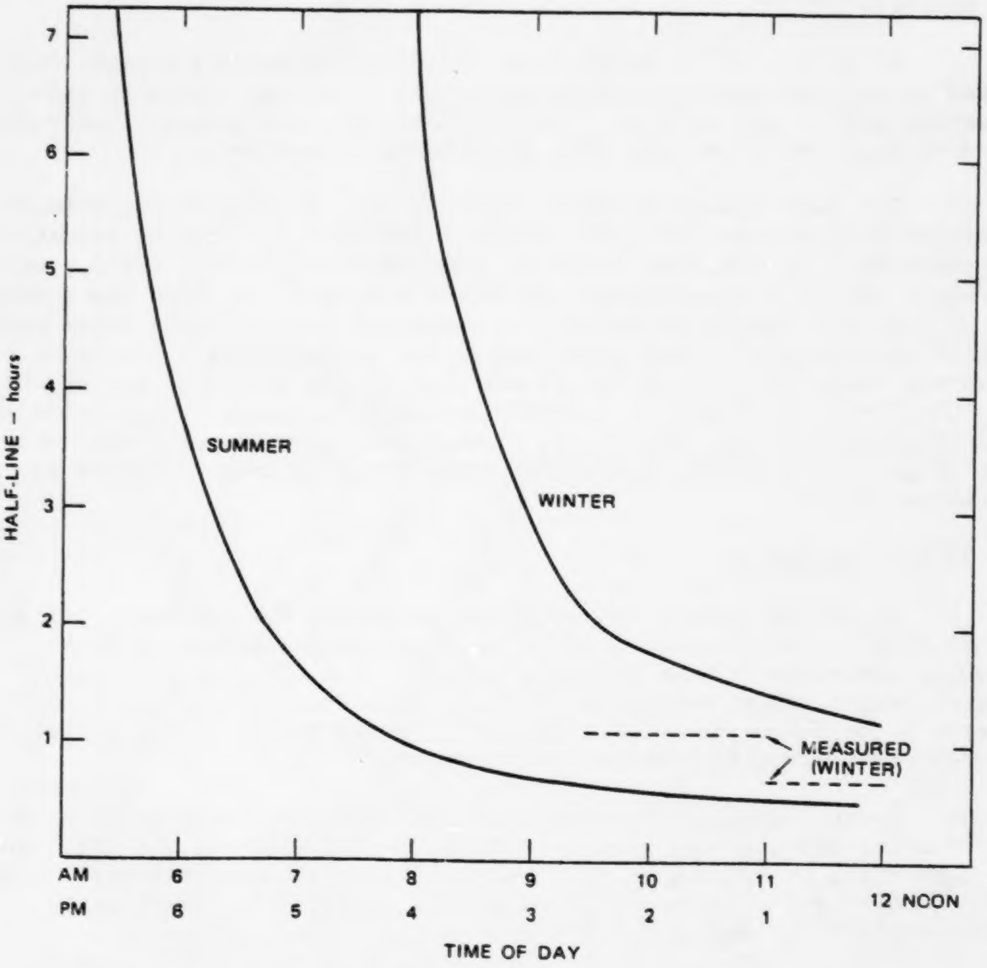

Figure 98-1 Seasonal and daily variation of the photolytic half-life of benzo[a]pyrene using the Zepp and Cline (1977) model. Data measured by Smith et al. (1978).

conducted similar studies on benzo[a]pyrene dissolved in acetone and adsorbed on calcium carbonate at several temperatures and with varying oxygen concentrations. Their findings tend to agree with those of McGinnes and Snoeyink (1974).

Lu et al. (1977) report that radiolabeled benzo[a]pyrene, dissolved in methanol and irradiated with light at 254 nm, produced rapid degradation with a half-life of 2 hours. Although this agrees closely with the data reported above, the role of methanol is unknown.

The data presented herein indicate that photolysis could be an important fate process for benzo[a]pyrene and other polycyclic aromatic hydrocarbons. As discussed later in this chapter, however, the log octanol/water partition coefficients for these compounds are high and a majority of them are readily adsorbed onto suspended matter. This means that in aquatic systems with a high suspended solids content (e.g., eutrophic lake) where the compounds will be mostly adsorbed to the suspended matter, the role of direct photolysis is probably not very important. Polycyclic aromatic hydrocarbons may, therefore, be more persistent in eutrophic waters than oligotrophic waters, since photolysis would be less effective in eutrophic waters.

98.4.2 Oxidation

In natural water, the principal oxidizing species are: (1) alkylperoxy ($RO_2\cdot$) radicals generated by the photolytic cleavage of trace carbonyl compounds or from enzymatic sources, and (2) singlet oxygen. Singlet oxygen, whose mechanism of action was discussed above, is considered to be the major oxidant species involved in the direct photolysis of polycyclic aromatic hydrocarbon molecules.

Several qualitative studies of free-radical oxidation of polycyclic aromatic hydrocarbons have been reported (NAS 1972; Tipson 1965) and are summarized by Radding et al. (1976). The rates of free radical oxidation by $RO_2\cdot$ vary among specific polycyclic aromatic hydrocarbons (Mahoney 1965) but depend for the most part on concentration of $RO_2\cdot$ radicals, which Radding et al. (1976) estimate to be a 10^{-10} molar steady-state concentration under average daily illumination in natural water systems.

Half-lives for the reaction of $RO_2\cdot$ radical with anthracene, benzo[a]pyrene, and perylene have been calculated to be 1600, 9900, and 1600 days, respectively (Radding et al. 1976). Although photolysis rate constants were not reported for benzo[ghi]perylene, dibenzo[a,h]anthracene or indeno[1,2,3-cd]pyrene, it appears probable that the half-lives for oxidation of these by $RO_2\cdot$ radical would be similar to those above (i.e., relatively long) and that faster processes must determine their probable aquatic fate.

The susceptibility of benzo[a]pyrene to free radical oxidation was examined by Smith et al. (1978) under experimental laboratory conditions. They obtained a pseudo first order rate constant ($k_{ox}(RO_2\cdot)$) of $5.7 \times 10^{-5} sec^{-1}$ for the oxidation of benzo[a]pyrene by $RO_2\cdot$ radical. Extrapolating to 25°C, this rate is translated into a second-order constant of $1.68 \times 10^3 M^{-1} sec^{-1}$ and assuming a "natural" concentration of $10^{-10}M$ for $RO_2\cdot$ radical, the half-life for oxidation of benzo[a]pyrene in aquatic environments is estimated to be around 4 days. Although this half-life is considerably shorter than that calculated by Radding et al. 1976, the free-radical oxidation of benzo[a]pyrene is still not competitive with photolysis or adsorption under environmental conditions (Smith et al. 1978).

Chlorine and ozone, when used in disinfecting drinking water, are strong oxidants which can chemically react with any polycyclic aromatic hydrocarbon present in the water to form quinones. Perry and Harrison (1977) studied the removal by chlorination of 8 polycyclic aromatic hydrocarbons including benzo[a]pyrene and indeno[1,2,3-cd]pyrene from water. Concentrations ranged from 30-860 ng/l, amounts normally encountered in raw water. With 2.2 mg/l free chlorine, pH-6.8 and 20°C,30 percent of indeno-[1,2,3-cd]pyrene and 50% of benzo[a]pyrene were degraded after 20 minutes contact time. Decreased pH and increased temperature both increased the rate of degradation. Data summarized by Radding et al. (1976) indicate that benzo[a]pyrene will have an initial ten-minute half-life when exposed to a 0.5 mg/l solution of chlorine in water (Trakhtman and Manita 1966). From observations of Il'nitskii et al. (1968), Radding et al. (1976) calculated the half-lives for benzo[ghi]perylene, pyrene, benzo[a]pyrene, benzo[a]anthracene oxidation by ozone in water to be approximately one minute. The chemical kinetics of chlorination of benzo[ghi]perylene in dilute aqueous solution was investigated by Harrison et al. (1976). The active chlorinating agent was hypochlorous acid, and a first order dependence of the reaction rate upon the concentration of the acid and benzo-[ghi]perylene was found. Benzo[ghi]perylene concentration was reduced by 50 percent when reacted with a 2.2 mg/l concentration of free chlorine at 20°C, pH of 6.8 for 15 minutes. These data indicate that oxidation by chlorine and ozone may be a significant fate process when these oxidants are available in sufficient quantity.

98.4.3 Hydrolysis

Polycyclic aromatic hydrocarbons, do not contain groups amenable hydrolysis. Hydrolysis, therefore, is not thought to be a significant fate process (Radding *et al*. 1976).

98.4.4 Volatilization

Several authors have suggested ways to estimate volatilization rates of compounds from water using theoretical considerations (Mackay and Wolkoff 1973; Mackay and Leinonen 1975). These methods, however, contain practical deficiencies which preclude their use in estimating the volatilization from natural waters. Measured volatilization rates for benzo[ghi]perylene, dibenzo[a,h]anthracene and indeno[1,2,3-cd]pyrene were not found in the literature, and an assessment of volatilization as a transport process from data measured for other polycyclic aromatic hydrocarbons is only speculative at this time.

Volatilization of benzo[a]pyrene was measured by Smith *et al*. (1978) using the theory and method offered by Tsivoglou (1967) and described by Hill *et al*. (1976). Smith *et al*. (1978) determined the benzo[a]pyrene volatilization half-life to be greater than 140 hours under the experimental conditions of rapid stirring. Using the same conditions, Smith *et al*. (1978) observed a half-life of 89 hours for benzo[a]anthracene during rapid stirring. Half-lives of 140 and 89 hours for volatilization are slow when compared to photolysis ($t_{1/2}$ about 1-2 hours). In addition, a large amount of the polycyclic aromatic hydrocarbons will be in the sorbed state which is thought to significantly reduce volatilization (Smith *et al*. 1978).

Lu *et al*. (1977), using a laboratory model ecosystem, studied the environmental fate and transport of radiolabeled benzo[a]pyrene. Their studies failed to detect any volatile radioactivity or $^{14}CO_2$ in traps from their aquatic microcosm, thus supporting the premise that benzo[a]pyrene is not significantly transported by volatilization.

In a laboratory study of a model stream 1.0 m in depth, Southworth (1979) measured the volatilization rates of several polycyclic aromatic hydrocarbons containing from 2 to 5 rings. He found for example that the volatilization rate decreases in general as the vapor pressure decreases, both of which are inversely related to the number of aromatic rings, and that the volatilization rate is highly dependent upon the mixing rates within both the water and associated air columns. Polycyclic aromatics containing fewer aromatic rings such as naphthalene and anthracene are also more sensitive to mixing within the water column than those containing a greater number of aromatic rings such as benzo[a]pyrene and benzo[a]-anthracene. For example, the volatilization half-life for naphthalene increased 7.5 times compared to 1.4 for benzo[a]pyrene following a 10 fold increase in stream flow velocity. The volatilization rate was less sensitive to changes in wind velocity but still increased up to 5 times for a 10 fold increase in velocity and the half-times for volatilization of naphthalene, anthracene, benzo[a]anthracene aznd benzo[a]pyrene with maximum wind velocity (4 m/sec) and stream current velocity (1 m/sec) were 3.2, 16, 150 and 430 hours respectively. Since these values represent the theoretically expected maximum, (not taking into account physical factors which slow evaporation such as sorption) Southworth (1979) concludes that the rate of vaporization of polycyclic aromatics with 4 or more rings will be insignificant under all conditions and the evaporation of lower molecular weight compounds such as naphthalene may be substantial only in a clear, rapidly flowing stream.

Volatilization of some high molecular weight, sparingly soluble organics has been shown to be surprisingly rapid due to exceptionally high activity coefficients (Mackay and Wolkoff 1973; Mackay and Leinonen 1975). Polycyclic aromatic hydrocarbons may have similarly high activity coefficients; however, based upon available data, volatilization does not appear to be an important transport process for these compounds in general.

98.4.5 Sorption

The data reviewed did not reveal specific partition coefficients of benzo[ghi]perylene, dibenzo[a,h]anthracene and indeno[1,2,3-cd]pyrene between water and suspended particulate matter or biota although considerable information is available for benzo[a]pyrene. Polycyclic aromatic hydrocarbons are widely distributed in the environment and are transported suspended onto particulate matter in air or water (NAS 1972; Radding *et al*. 1976). The calculated log octanol/water partition coefficients based on the method of Leo *et al*. (1971) range from 7.66 for indeno[1,2,3-cd]pyrene to 5.97 for dibenzo[a,h]anthracene based on the method of Leo *et al*. (1971) indicating that these compounds should be strongly adsorbed onto suspended particulate matter, especially particulates high in organic content.

In agreement with this assumption, benzo[a]pyrene and benzo[a]-anthracene, with log octanol/water partition coefficients of 6.31 and 5.61, respectively, do show rapid partitioning onto suspended matter (Smith *et al*. 1978). These authors report partition coefficients (Kp) of 150,000 for benzo[a]pyrene and 21,000 for benzo[a]anthracene between water and sediment containing 5 percent organic carbon, thus indicating that sorption onto sediments is strongly correlated with the organic carbon levels in sediments. Using a one-compartment model which simulates river conditions, Smith *et al*. (1978) predict that 83 percent of benzo[a]pyrene and 71 percent of benzo[a]anthracene will be sorbed onto the suspended solids present in the simulated river. Figure 98-2 illustrates the sorption isotherms of benzo[a]pyrene with various types of sediments and Figure 98-3 shows the effect of suspended solids on benzo[a]pyrene when discharged to a hypothetical mixed river system. The experimental work performed by Smith et al. (1978) also shows that both benzo[a]anthracene and benzo[a]pyrene are strongly adsorbed onto bacterial cells as well as suspended abiotic particulate matter.

Southworth (1977) showed that anthracene (log octanol/water partition coefficient of 4.45) was sorbed strongly by suspended particulates containing autoclaved yeast cells as the organic fraction. A partition coefficient (solids/water) of approximately 25,000 was observed which is indicative of a strong tendency for anthracene to be biosorbed. Sorption by inorganic particulates was less and resulted in a partition coefficient of 1600.

These data indicate that the polycyclic aromatic hydrocarbons cited above, will accumulate in the sediment, and biota portions of the aquatic environment and that adsorption is probably their dominant aquatic transport process.

98.4.6 Bioaccumulation

A large number of polycyclic aromatic hydrocarbons have been identified in living matter, and data collected from field and laboratory studies indicate that organisms throughout the phylogenetic scale can incorporate and metabolize them (Radding et al. 1976). Specific data on the bioaccumulation of benzo[ghi]perylene, dibenzo[a,h]anthracene and indeno-[1,2,3-cd]pyrene were not found, and conclusions for them therefore are based on data for benzo[a]pyrene or polycyclic aromatic hydrocarbons as a group. Since these compounds appear to have a relatively high (calculated) log octanol/water partition coefficient (log P), and since most theoretical and empirical data indicate compounds with high log P values tend to accumulate in biota (Neely et al. 1974), polycyclic aromatic hydrocarbons with 5 or more aromatic rings probably will be bioaccumulated.

Southworth et al. (1978) determined the bioaccumulation potential of seven polycyclic aromatic hydrocarbons including naphthalene, anthracene, phenanthrene, pyrene, 9 methylanthracene, benzo[a]anthracene and perylene in *Daphnia pulex*. All were rapidly taken up with naphthalene and anthracene reaching an equilibrium within 2 and 6 hours respectively and benzo[a]anthracene in 24 hours. The equilibrium concentration factors increased dramatically with increasing molecular weight ranging from 100

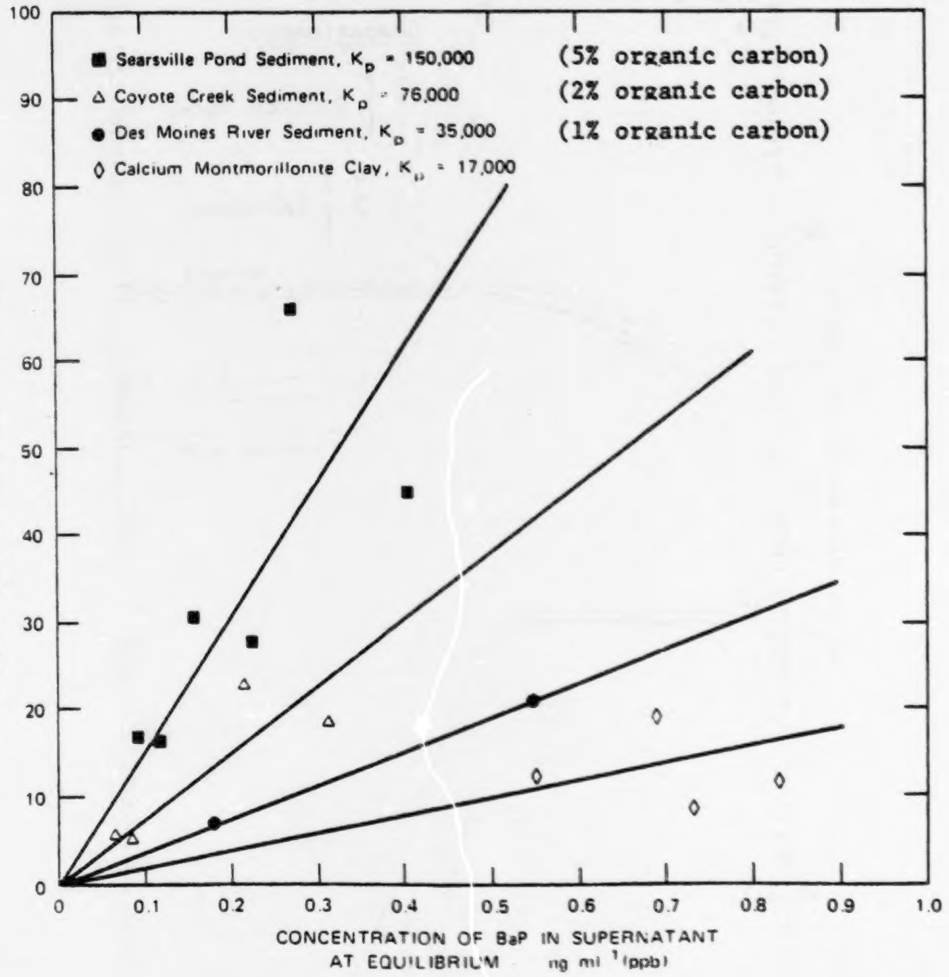

Figure 98-2 Sorption isotherms of benzo[a]pyrene. From Smith *et al.* (1978).

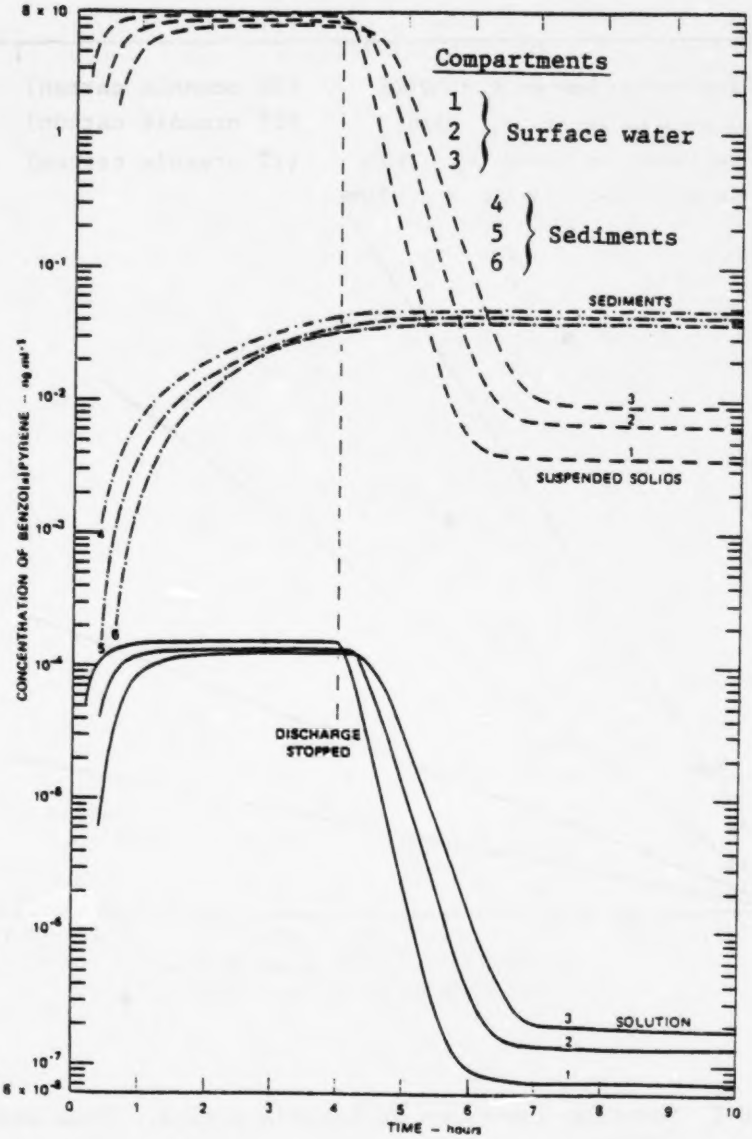

Figure 98-3 Effect of suspended solids on benzo[a]pyrene in a partially mixed, modeled river system. Taken from Smith et al. (1978).

or naphthalene to 10,000 for benzo[a]anthracene. The calculated n-octanol/water partition coefficients were found to be good predictors of bioaccumulation potential in Daphnia. The rapid bioaccumulation suggests that body burdens in zooplankton will follow closely the aqueous concentration of polycyclic aromatics and not be dependent upon food chain.

Lu et al. (1977) measured the uptake of benzo[a]pyrene by fish, mosquito, and snails. The organisms were placed separately into 1-gal wide-mouthed jars containing 1 liter of standard reference water and radiolabeled ^{14}C benzo[a]pyrene at 0.0025 mg/l. Aliquots of the organisms were collected after 1, 2 and 3 days exposure to the benzo[a]pyrene, washed, weighed, and assayed for total reactivity. Little degradation of benzo(a)]yrene occured in the snail with 88 percent of the total ^{14}C accumulated after 3 days being associated with the parent compound. On the other hand, only 22 percent remained in the mosquito larvae and 0 percent in the fish after 3 days. The bioconcentration factor (benzo[a]pyrene in organism/benzo[a]pyrene in water) after 3 days was 37x in the mosquito and 2177x in the snail. Lu et al. (1977) state that the fish detoxifies benzo-[a]pyrene about as rapidly as it is adsorbed and converts it to unextractable products.

In the laboratory microcosm experiments described in detail in section 98.4.8, Lu et al. (1977) showed that benzo[a]pyrene was bioconcentrated and stored in substantial amounts in the tissues of organisms growing in an aquatic microcosm. The biomagnification factors in the food chain were: fish, 930; algae, 5258; mosquito, 11,536; snail, 82,231; and daphnia, 134,248. In addition, Smith et al. (1978) found the sorption of benzo[a]pyrene onto bacterial cells to be rapid with a partition coefficient (cell/water) of approximately 10^4 (Smith et al. 1978).

Bioaccumulation data for other polycyclic aromatic hydrocarbons (Anderson 1978; Hase and Hites 1976; Lee et al. 1972; Niaussat and Auger 1970; Scaccini-Cicatelli 1966; Southworth 1977) parallel the results of Lu et al. (1977). Although polycyclic aromatic hydrocarbons are rapidly bioaccumulated, they are also rapidly metabolized and eliminated (excreted) from the organism. Bioaccumulation, especially in vertebrate organisms, is considered to be short-term, and is probably quite unlike the long-term bioaccumulation that has been demonstrated for some of the more persistent chlorinated organics (e.g., polychlorinated biphenyls and DDT). Thus, bioaccumulation in multi-cellular organisms is not considered an important fate process. The sorption of benzo[a]pyrene and probably benzo[ghi]perylene, dibenzo[a,h]anthracene and indeno[1,2,3-cd]pyrene onto suspended biota (e.g., algae cells) and abiotic matter does, however, appear to be the most important transport process.

98.4.7 Biotransformation and Biodegradation

The degradation and metabolism of polycyclic aromatic hydrocarbons and the identification of their metabolites are known from studies conducted with bacteria and mammals, and are summarized by the National Academy of Sciences (1972) and Radding *et al*. (1976). In mammals, the major metabolites of polycyclic aromatic hydrocarbons are hydroxylated derivatives and epoxides (Sims 1970); degradation by mammals, however, is considered incomplete with the parent compound and the metabolites being excreted via the urinary system (Evans *et al*. 1965).

Bacteria have been shown to utilize some polycyclic aromatic hydrocarbon compounds as a sole carbon source for growth, and evidence summarized by Radding *et al*. (1976) suggest that bacteria can degrade polycyclic aromatic hydrocarbon compounds much more completely than mammals. Evidence for bacterial degradation comes from studies conducted on only a few compounds; data specific to benzo[ghi]perylene, dibenzo[a,h]-anthracene and indeno[1,2,3-cd]pyrene were not found and conclusions are, therefore, based on biodegradation studies conducted for benzo[a]pyrene and other selected polycyclic aromatic hydrocarbons.

Anderson (1978) developed a sensitive *in vitro* method to quantify the production of radiolabeled benzo[a]pyrene derivatives by the American oyster (*Crassotrea virginica*) aryl hydrocarbon hydroylase (AHA), an enzyme system associated with the liver in mammals and digestive cells in invertebrates. His work provides evidence that oyster AHA catalyzes the production of a variety of biologically active and inactive benzo[a]pyrene metabolites including dihydrodiols, quinones, and hydroxy derivatives. Quinones were the major metabolites in normal oysters; the production of hydroxy derivatives was particularly stimulated by PCB induction. Anderson's data showed that after an initial burst of oyster AHA activity there is a steady production of metabolites for at least 60 minutes under the environmental test conditions; one-half of the total metabolites were produced in 20 minutes.

The metabolism of benzo[a]pyrene in the salt marsh caterpillar was studied by Lu *et al*. (1977). Caterpillar larvae (4th instar) were first fed a moth medium containing ^{14}C-benzo[a]pyrene. After the treated medium was consumed it was given *ad libitum.* After 24 hours, feces and body were separated, homogenized, extracted, and assayed for total radioactivity. The results show that the caterpillars excreted most of the radiolabeled benzo[a]pyrene as fecal products; one-half of the radioactivity was present as the parent compound, with the remainder as polar metabolites.

Using rat liver homogenates, Sims (1970) conducted *in vitro* tests of benzo[a]pyrene metabolism and isolated the following metabolites: the monophenols (3-and 6-hydroxy-), the diphenols (3,6- and 1,6-dihydroxy-), the corresponding quinones (3,6-dione and 1,6-dione) and 2-dihydrodiols (1,2-and 9',10-).

The metabolism of benzene, naphthalene, phenanthrene and anthracene is accomplished by a broad spectrum of bacteria, and pathways for these processes have been reported by Zobell (1946) and Ribbons (1965). By contrast, however, there is not much known about bacterial metabolism of other polycyclic aromatic hydrocarbons. Common enrichment-culture techniques cannot be used to obtain organisms able to grow on the larger polycyclic aromatic hydrocarbons as sole carbon sources since these compounds are essentially insoluble in water and will either not support growth or growth may be extremely slow (Barnsley 1975). This problem has been somewhat overcome by using other carbon sources to stimulate (or induce) bacterial production. Sisler and Zobell (1947) were able to isolate bacteria (which were grown on other carbon sources) that degraded 1,2-benzanthracene and 1,2,5,6-dibenzanthracene; Poglazova *et al*. (1972) and Lorbacher *et al*. (1971) achieved similar results with benzo[a]pyrene. The maximum rate of disappearance of benzo[a]pyrene in cultures of *E. coli* calculated by Barnsley (1975) from the data of Lorbacher *et al*. (1971) is about 0.02 μM hr^{-1} or 0.2×10^{-3} μmol hr^{-1}mg^{-1} bacterial protein. The maximum rate of metabolism of benzo[a]pyrene by *Pseudomonas* NCIB 9816 observed by Barnsley (1975) was 0.13 μM hr^{-1} or 0.9×10^{-3} μmol hr^{-1}mg^{-1} bacterial protein. This rate is intermediate between those computed from the results of other workers (Barnsley 1975).

Studies by Gibson *et al*. (1975) show that certain microbes convert benzo[a]pyrene to *cis*-9, 10-dihydroxy-9,10-dihydrobenzo[a]pyrene; more extensive degradation was achieved with the bacterium *Beijerenckia* isolated from a polluted stream. The wild strain of *Beijerenckia* was obtained by enrichment cultures using biphenyl as the sole source of carbon for growth. This work indicates the possible value of using chemically related products for development of enrichment cultures.

Data presented by Smith *et al*. (1978) seem to indicate that long-term exposure of microbes is necessary before a bacterial population is capable of degrading polycyclic aromatic hydrocarbons. Their work with three sets of experimental conditions used in attempting to develop enrichment cultures to degrade benzo[a]pyrene and benzo[a]anthracene failed to yield systems capable of significant biodegradation. They surmise that there is a natural preselection and induction process that occurs under natural conditions and that their experimental conditions did not allow for the proper induction period.

Herbes and Schwall (1978) found that naphthalene (half-time 5.0 hours) and anthracene (half-time 280 hours) are degraded rapidly in hydrocarbon contaminated sediment samples. The half-times for polycyclic aromatic hydrocarbons containing 4 or more rings however, were much longer (benzo[a]anthracene, 7,000 hours and benzo[a]pyrene 21,000 hours) causing these authors to suggest that such compounds may persist even in sediments that have received chronic polycyclic aromatic hydrocarbon inputs. In addition, half-times in samples obtained from uncontaminated streams were 10 to 400 times longer than those from contaminated streams.

Southworth (1977) reports the rate of microbial degradation of anthracene to be 0.0612 hr^{-1} with a corresponding half-life of 11.3 hours. His work differs from Smith et al. (1978) in that he collected water, with its attendant microbial population, from a small stream that was known to be chronically affected by industrial effluents containing anthracene. Southworth (1977) summarized his findings by stating that the persistence of anthracene in natural waters under summer conditions of temperature and illumination appears to be primarily determined by the fate processes of photolysis and degradation by microorganisms suspended in the water column. Furthermore, he reports that in large, deep (5 m), slow moving rivers, such as the upper Ohio, depth and turbidity would act to reduce the importance of photolysis, making microbial activity the major fate process.

Evans et al. (1965) reports that phenanthrene is metabolized by soil Pseudomonads to 1,2-dihydroxynaphthalene via several steps involving hydroxylated intermediates. Data presented by Lorbacher et al. (1971), Shabad (1968), Fedoseeva et al. (1968) and others demonstrate that soil microbes are capable of degrading certain polycyclic aromatic hydrocarbons, primarily 3,4-benzopyrene, anthracene, and phenanthrene, and that the rate and degree of degradation is greatest when the soil and its microbial population have acclimated to them. Soil systems are known to provide much better conditions for biodegradation than aquatic systems. Poglazova et al. (1972) report that indigenous bacteria of power plant and coke oven wastewater effluents contaminated with 3,4-benzopyrene metabolized less than 15 percent of the compound.

The data presented herein seems to point in the direction of biodegradation as an important fate process for polycyclic aromatic hydrocarbons in general. Biodegradation of compounds with 4 or more rings is much slower than the tricyclic compounds. Biodegradation is probably slower in the aquatic system than in the soil, and biodegradation may be much more important in those aquatic systems which are chronically affected by polycyclic aromatic hydrocarbon contamination.

98.4.8 Microcosm Studies, Field Studies, and Modelling

Radiolabeled benzo[a]pyrene (benzidine and vinyl chloride were also studied) was evaluated in laboratory model ecosystems for environmental fate, degradation pathways, bioconcentration, and food chain accumulation by Lu *et al*. (1977). Two types of model ecosystem (microcosm) experiments were performed; a closed model aquatic ecosystem and a terrestrial-aquatic model ecosystem. A detail description of these model ecosystems is provided by Lu and Metcalf (1975) and Metcalf (1974).

In the closed aquatic system, ^{14}C-benzo[a]pyrene was directly applied to the water at 0.002 mg/l and allowed to pass through a food chain of plankton, filamentous green algae (*Oedogonium cardiacum*), daphnia (*Daphnia magna*), mosquito larva (*Culex pipieus*), snail (*Physa sp*.), and mosquito fish (*Gambusia affinis*). Fate and transport were observed over a three-day period at 26.7°C in an environmental chamber under 750 ft.-candle illumination. The radioactivity was monitored throughout the experimental period by liquid scintillation. At the conclusion of the experiments, one liter of water was extracted and the organisms homogenized; the extract was then concentrated, the ^{14}C content evaluated, and relative amounts of degradation products determined by various analytical techniques (Lu *et al*. 1977).

The results of the aquatic microcosm study show that benzo[a]pyrene was bioconcentrated and stored in substantial amounts in the tissues of all organisms where the parent compound represented from 46 percent of the total extractable ^{14}C in mosquito larvae to 90 percent in daphnia. The biomagnification factors were: fish, 930; algae, 5258; mosquito, 11,536; snail, 82,321; and daphnia, 134,248 (Lu *et al*. 1977). The benzo[a]pyrene was degraded to unknown polar compounds which they presumed to be hydroxylated derivatives. It appears likely that the high level of benzo[a]pyrene found in the fish is a reflection of food chain transfer (biomagnification) since an uptake study with benzo[a]pyrene (discussed previously) did not reveal bioaccumulation in fish tissue.

In the terrestrial-aquatic model ecosystem, 0.2 mg of ^{14}C-benzo[a]pyrene was topically applied in an acetone solution to *Sorghum vulgare* seedlings at the terrestrial end to simulate atmospheric fall out. The plants were then consumed by salt marsh caterpillar larvae (*Estigmene acrea*) and the ^{14}C-labeled products entered the terrestrial and aquatic phases as fecal products, leaf grass, etc. The food chain organisms in the model ecosystem were the same as in the model aquatic system. The radioactive products were allowed to interact in the system over a 33-day period at 26.7°C with a 12-hr diurnal cycle and 5,000 ft.-candle illumination. Water samples were collected and analyzed as described above for the aquatic ecosystem (Lu *et al*. 1977).

The 33-day terrestrial-aquatic model ecosystem provided for a longer degradation period and food chain transfer than the 3-day aquatic system. The amount of benzo[a]pyrene in the aquatic phase reached a maximum level of 0.005 ppm (determined by radioactivity and expressed as ppm equivalents) after 14 days and declined to 0.00344 ppm at the conclusion of the experiment at 33 days. The parent ^{14}C-benzo[a]pyrene comprised 7.1 percent of the total extractable ^{14}C in fish (ecological magnification, E.M., of 30), 19 percent snail (E.M. 4860), 32 percent in algae (E.M. 31610) and 34 percent in mosquito (E.M. 2120).

Lu *et al*. (1977) found traces of several unknown degradation products although most were found as polar products. In both microcosms, the *in vivo* degradation of benzo[a]pyrene was by hydroxylation and conjugation to produce highly polar derivatives.

98.5 Data Summary

The results of the data review indicate that benzo[a]pyrene and probably benzo[ghi]perylene, dibenzo[a,h]anthracene and indeno[1,2,3-cd]pyrene will accumulate in the sediment and biota and will be transported with the suspended sediment. Some amount will be dissolved and be degraded by direct photolysis. The ultimate fate of the dissolved polycyclic aromatic hydrocarbons however, is believed to be biodegradation and transformation by benthic organisms, microbes, and vertebrate organisms in the food chain.

The half-lives of dissolved benzo[a]pyrene, calculated by Smith *et al*. (1978) for individual fate and transport processes following a spill are shown in Table 98-1. Although the half-lives vary among types of aquatic systems, sorption dominates as the primary transport process. The role of biodegradation and transformation is not well represented in the table since Smith *et al*. (1978) were not able to develop degrading cultures.

Summaries of the data discussed above are presented in Tables 98-2.1 through 98-2.4. Very little data specific to benzo[ghi]perylene, dibenzo[a,h]anthracene and ideno[1,2,3-cd]pyrene were found, and rates or half-lives for other non-specific polycyclic aromatic hydrocarbons are not presented in the table. The summary statement presented in each table is, for the most part, taken from fate data which apply to polycyclic aromatic hydrocarbons in general. The information for benzo[a]pyrene is, however, reasonably complete.

Table 98-1 Transport and fate of Benzo[a]pyrene predicted by a one-compartment model (Smith *et al*. 1978)

Process	Stream	Eutrophic Pond	Eutrophic Lake	Oligotrophic Lake
Photolysis, $t_{1/2}$ in hrs.	3	7.5	7.5	1.5
Oxidation, $t_{1/2}$ in hrs.[1]	>340	>340	>340	>340
Volatilization, $t_{1/2}$ in hrs.	>140	>350	>700	>700
Hydrolysis, $t_{1/2}$ in hrs.	Large	Large	Large	Large
Biodegradation, $t_{1/2}$ in hrs.	Large	Large	Large	Large
$t_{1/2}$ for all processes (except dilution) in hrs.	2.9	7.3	7.4	1.5
$t_{1/2}$ for all processes (including dilution) in hrs.	0.48	7.3	7.4	1.5
Amount of sorbed compound (mg M^{-3})	5	15	2.5	2.5
Percentage sorbed	83%	93%	71%	71%

[1] Based on a peroxy radical concentration of 10^{-10} M.

Table. 98-2.1

Summary of Aquatic Fate of Benzo[ghi]perylene

Environmental Process[a]	Summary Statement[b]	Rate	Half-Life ($t_{1/2}$)	Confidence of Data[c]
Photolysis	Dissolved portion may undergo rapid photolysis.			
Oxidation	Oxidation of PAH by RO_2 radical is slow; not a significant process.			
Hydrolysis	PAHs do not contain groups amenable to hydrolysis.			
Volatilization	Is probably not as important as adsorption as a transport process.			
Sorption	Measured adsorption coefficients for PAH and suspended solids are high; movement in sediment considered the most important transport process.			
Bioaccumulation	A short-term process; PAH's are metabolized slowly and long-term partitioning into biota is not a significant fate process.			
Biotransformation/ Biodegradation	PAHs with 4 or more aromatic rings are degraded slowly by microbes and are readily metabolized by multi-cellular organisms; biodegradation is probably the ultimate fate process.			

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. Very little environmental fate data specific to benzo[ghi]perylene were found; the summary statement is made from data reviewed for PAHs as a group.

c. Data on benzo[ghi]perylene are not sufficient to permit confidence ranking. The confidence of the data reviewed for PAHs in general ranges from low to high.

Table 98-2.2

Summary of Aquatic Fate of Benzo[a]pyrene

Environmental Process[a]	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Dissolved portion may undergo rapid photolysis.	$2.8 \times 10^{-4} sec^{-1}$	1-2 hrs.	Medium
Oxidation	Oxidation of PAH by RO radicals is slow; not a significant process.	$1.68 \times 10^{3} M^{-1} sec^{-1}$	96 hrs.	Medium
Hydrolysis	PAHs do not contain groups amenable to hydrolysis.	0	-	High
Volatilization	Is probably not as important as adsorption as a transport process.	$3 \times 10^{2} hr^{-1}$	22 hrs.	Medium
Sorption	Measured adsorption coefficients for PAH and suspended solids are high; movement in sediment is considered to be the most important transport process.	150,000	-	Medium
Bioaccumulation	A short-term process; PAHs with 4 or more aromatic rings are slowly metabolized and long-term partitioning into biota is not a significant fate process.	-	-	Medium
Biotransformation/ Biodegradation	PAHs with 4 or more aromatic rings are slowly degraded by microbes and are slowly metabolized by multicellular organisms; biodegradation is probably the ultimate fate process.	$0.2 - 0.9 \mu mol^{-1} mg^{-1}$	bacterial protein	Medium

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[a] There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

Table 98-2.3

Summary of Aquatic Fate of Dibenzo[a,h]anthracene

Environmental Process[a]	Summary Statement[b]	Rate	Half-Life ($t_{1/2}$)	Confidence of Data[c]
Photolysis	Dissolved portion may undergo rapid photolysis.			
Oxidation	Oxidation of PAH by RO_2 is slow; not a significant process.			
Hydrolysis	PAHs do not contain groups amenable to hydrolysis.			
Volatilization	Is apparently not as important a transport process as adsorption.			
Sorption	Measured adsorption coefficients for PAH and suspended solids are high; movement in suspended sediment is considered to be most important transport process.			
Bioaccumulation	A short-term process; PAHs with 4 or more aromatic rings are slowly metabolized and long-term partitioning into biota is not a significant fate process.			
Biotransformation/ Biodegradation	PAHs with 4 or more aromatic rings are slowly degraded by microbes and metabolized by multi-cellular organisms; biodegradation is probably the ultimate fate process.			

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. Very little environmental fate data specific to dibenzo[a,h]anthracene were found; the summary statement is made from data reviewed for PAHs as a group.

c. Data on dibenzo[a,h]anthracene are not sufficient to permit confidence ranking. The confidence of the data reviewed for PAHs in general ranges from low to high.

Table 98-2.4

Summary of Aquatic Fate of Indeno[1,2,3-cd]pyrene

Environmental Process[a]	Summary Statement[b]	Rate	Half-Life ($t_{1/2}$)	Confidence of Data[c]
Photolysis	Dissolved portion may undergo photolysis.			
Oxidation	Oxidation of PAH by RO_2 radical is slow; not a significant process.			
Hydrolysis	PAHs do not contain groups amenable to hydrolysis.			
Volatilization	Is probably not as important as adsorption as a transport process.			
Sorption	Measured adsorption coefficients for PAH and suspended solids are high; movement in sediment is considered to be the primary transport process.			
Bioaccumulation	A short-term process; PAHs with 4 or more aromatic rings are slowly metabolized and long-term partitioning into biota is not a significant fate process.			
Biotransformation/ Biodegradation	PAHs with 4 or more aromatic rings are slowly degraded by microbes and are metabolized by multicellular organisms; degradation is probably the ultimate fate process.			

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

b. Very little environmental fate data specific to indeno[1,2,3-cd]pyrene were found; the statement is made from data reviewed for PAHs as a group.

c. Data on indeno[1,2,3-cd]pyrene are not sufficient to permit confidence ranking. The confidence of the data reviewed for PAHs in general ranges from low to high.

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SECTION X: NITROSAMINES AND MISCELLANEOUS COMPOUNDS

Chapters 99-105

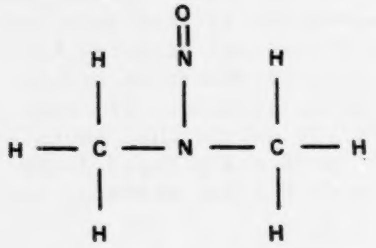
99. DIMETHYLNITROSAMINE

99.1 Statement of Probable Fate

Based on the relatively few pertinent data found, the most probable fate of dimethylnitrosamine in the aquatic environment appears to be slow photolytic degradation. Neither volatilization nor sorption processes appear to be important transport mechanisms. Bioaccumulation probably does not occur and, in the event that some of the pollutant should enter into the atmosphere, rapid photodegradation will take place. Dimethylnitrosamine exhibits resistance to microbial degradation, oxidation, and hydrolysis.

99.2 Identification

Dimethylnitrosamine has been detected in the atmosphere of metropolitan areas (Fine and Rounbehler 1976), and it may occur elsewhere in the environment (Ayanaba *et al.* 1973; Ayanaba and Alexander 1974; Mills and Alexander 1976; Mirvish *et al.* 1976). The chemical structure of dimethylnitrosamine is shown below.



Dimethylnitrosamine

CAS NO. 62-75-9
TSL NO. IQ 05250

Alternate Names

N-Nitrosodimethylamine
N-Methyl-N-nitrosomethanamine

99.3 Physical Properties

The general physical properties of dimethylnitrosamine are as follows.

Molecular weight (Windholz 1976)	74.08
Melting point	No data found
Boiling point at 760 torr (Windholz 1976)	151-153°C

Vapor pressure	No data found
Solubility in water (Mirvish *et al*. 1976)	Miscible
Log octanol/water partition coefficient (Radding *et al*. 1977)	0.06

99.4 Summary of Fate Data

99.4.1 Photolysis

Dimethylnitrosamine absorbs strongly in the near ultraviolet spectral region at 330 nm with significant absorption occurring up to 400 nm (Polo and Chow 1976). Although dialkylnitrosamines are reported to be relatively stable toward photolysis in neutral aqueous solutions (Chow 1964; Burgess and Lavanish 1964), Polo and Chow (1976) have demonstrated a slow photolytic decomposition (initial concentration at 74 mg/l) in aerated distilled water that exhibited zero order kinetics and had a half-life of 79 hours. The observed rate was shown to be dependent on the intensity of irradiation and the design of the apparatus. Chow (1973) has pointed out that the dialkylnitrosamines are photolabile only in dilute acids (pH >1) and that actual protonation of the nitrosamine in strong acids impedes photolysis. Chow's (1973) interpretation of this observation is that hydrogen bonding at the nitroso oxygen atom (rather than protonation) produces the photolabile intermediate; he further speculates that coordination of the nitrosamine with metal cations might also induce photolability. If these speculations should prove to be valid, the possibility exists that photolysis in environmental surface waters could lead to moderately rapid degradation of dimethylnitrosamine via hydrogen bonding with humic acids or coordination with metal cations.

In apparent contrast to the results of Chow (1973), MacNaughton and Stauffer (1975) report a half-life of approximately three hours for photolysis of dimethylnitrosamine (200 mg/l) when the solutions are exposed to direct sunlight in covered petri dishes. The solutions, however, were not buffered; and inasmuch as distilled water becomes slightly acidic upon storage due to absorption of atmospheric carbon dioxide, the conditions of this latter photolysis experiment were probably acidic. Indeed, the addition of sodium hydroxide in their experiments greatly reduced the rate of degradation of dimethylnitrosamine in sunlight.

It is uncertain whether volatilization from water will be a significant transport mechanism for dimethylnitrosamine. In the event that some of the pollutant should enter into the atmosphere, it is reported that it will be photolyzed rapidly with a half-life of less than one hour (Hanst *et al*. 1977; Radding *et al*. 1977).

99.4.2 Oxidation

No information that would support any role for oxidation as an environmental fate process was found in the reviewed literature. Tate and Alexander (1975) have reported that dimethylnitrosamine, which had been dissolved at a concentration of 20 mg/l in samples of water (pH 8.2) collected from Cayuga Lake, New York, persisted without change over an observed period of 3.5 months in the absence of light. The samples were open to the atmosphere and well-stirred, thus ensuring a constant supply of atmospheric oxygen.

99.4.3 Hydrolysis

Nitrosamines, in general, are hydrolytically stable at ambient environmental conditions and are reported to be hydrolyzed only at elevated temperatures in strongly acidic solutions (Fieser and Fieser 1956). Tate and Alexander (1975) reported no hydrolytic degradation of dimethylnitrosamine in Cayuga Lake water over an observation period of 3.5 months.

99.4.4 Volatilization

Although dimethylnitrosamine has a boiling point of 151-153°C at atmospheric pressure, it is completely miscible with water and it is apparently highly solvated (Chow 1973). MacNaughton and Stauffer (1975) report a half-life with respect to volatilization from distilled water in a petri dish of 3 to 6 hours at an initial concentration of 200 mg/l. The results of Tate and Alexander (1975) with Cayuga Lake water indicated that volatilization, if it occurred, was very slow in comparison to the 3.5 month period of observation. The water samples were well stirred and maintained at 30°C during this time. It should be noted that in the experiments of MacNaughton and Stauffer (1975) the concentration of dimethylnitrosamine never fell below 20 mg/l even though the water-depth in the petri dish did not exceed one centimeter. The rate of volatilization from water of highly solvated molecules becomes very slow compared to the rate of volatilization of the water itself at very dilute concentrations of the solute molecule. It is quite likely that, in the absence of photolytic degradation, dimethylnitrosamine could be highly persistent at the levels of pollutant concentration expected to be found in the aquatic environment.

99.4.5 Sorption

The octanol/water partition coefficient is near unity as shown by both the reported value of log P = 0.06 (Radding et al. 1977) and the calculated value of log P = -0.69 from the data of Mirvish et al. (1976). There is apparently no significant preference for either aqueous or organic media and thus sorption by organic particulates should not be an important partitioning process. Dean-Raymond and Alexander (1976) observed that dimethylnitrosamine and sodium chloride both exhibited the same mobility in a column of wet soil (Williamson silt loam) indicating that dimethylnitrosamine may not be sorbed by either organic or clay particulates in an aqueous medium.

99.4.6 Bioaccumulation

The combination of low partition coefficient and complete miscibility with water indicates little potential for bioaccumulation. No specific information regarding bioaccumulation was found in the reviewed literature.

99.4.7 Biotransformation and Biodegradation

Tate and Alexander (1975) have reported that no biodegradation of dimethylnitrosamine was observed in their lake water samples during an observation period of 3.5 months, and that a lag of nearly 30 days occurred before its slow disappearance from soil. The nitrosamine appeared to be degraded very slowly in sewage, but it was not affected by the anaerobic organisms of bog sediments collected in a New York wildlife refuge (Tate and Alexander 1976).

99.5 Data Summary

Table 99-1 summarizes the aquatic fate data discussed above for dimethylnitrosamine. Photolysis in aqueous solution, and perhaps to a limited extent in the atmosphere, appears to be the major degradative process. At the pollutant levels expected to be found in the aquatic environment, neither volatilization nor sorption processes appear to be important. Dimethylnitrosamine exhibits resistance to microbial degradation and, in the absence of photolysis, it could have an appreciable life time.

Table 99-1

Summary of Aquatic Fate of Dimethylnitrosamine

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis[a]	Slow photolysis appears to be the only fate process of any consequence.	—	—	Medium
Oxidation	Probably not important.	-	-	Low
Hydrolysis	Probably not important.	-	-	Low
Volatilization	Probably not important.	-	-	Low
Sorption	Probably not important.	-	-	Low
Bioaccumulation	Probably not important.	-	-	Low
Biotransformation/ Biodegradation	Slow degradation is reported to occur in sewage and soil, but this pollutant appears to be resistant to biodegradation in surface waters.	-	-	Medium

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a. The predominant environmental process which is thought to determine the fate of the compound.

99.6 Literature Cited

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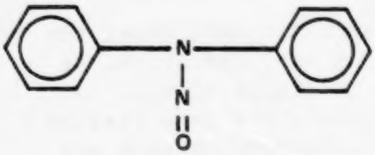
100. DIPHENYLNITROSAMINE

100.1 Statement of Probable Fate

Based on the relatively few pertinent data found, the most probable fate of diphenylnitrosamine in the aquatic environment cannot be determined at this time. Photolytic degradation may be important, and sorption processes may be operative as transport mechanisms; but oxidation, hydrolysis, and volatilization do not appear to affect the aquatic fate. Diphenylnitrosamine is both more easily synthesized and degraded by microorganisms than are dialkylnitrosamines.

100.2 Identification

The chemical structure of diphenylnitrosamine is shown below.



Diphenylnitrosamine

CAS NO. 86-30-6
TSL NO. JJ 98000

Alternate Names

N-Nitroso-N-phenylbenzamine
N-Nitrosodiphenylamine

100.3 Physical Properties

The general physical properties of diphenylnitrosamine are listed below.

Molecular weight (Tanikaga 1969)	198.24
Melting point (Tanikaga 1969)	66.5°C
Boiling point	No data found
Vapor pressure	No data found
Solubility in water	No data found
Log octanol/water partition coefficient (Calc. by method of Leo *et al.* 1971 from the data of Mirvish *et al.* 1976).	2.57

100.4 Summary of Fate Data

100.4.1 Photolysis

The ultraviolet absorption maximum for diphenylnitrosamine occurs at 292 nm with significant absorption continuing to 400 nm (Tanikaga 1969; Polo and Chow 1976). Thus, the compound appears capable of light absorption sufficient to cause photolysis in aqueous solution, although no specific rates or other data concerning this process were found. Irradiation of an ethanolic solution of diphenylnitrosamine (10^{-2}M) for 3 hours through a Pyrex filter (λ >290 nm) yielded primarily diphenylamine plus small amounts of 4-nitrosodiphenylamine, 4-nitrodiphenylamine, 2-nitrodiphenylamine, and carbazole (Tanikaga 1969). The irradiation of a saturated solution of diphenylnitrosamine under the same conditions also gave tetraphenylhydrazine. The reaction products can be rationalized best by homolytic N-N bond fission to give a nitrosyl radical and a diphenylaminium radical which then lead to the observed products (Tanikaga 1969).

Water is not as good a hydrogen atom donor as ethanol under environmental conditions, and the product distribution may, therefore, be quite different in water than what was observed by Tanikaga (1969). At highly dilute concentrations in an aqueous environment, N-N bond fission can still be expected to occur, but the fate of the diphenylaminium and nitrosyl radical would depend greatly on the presence and nature of other organic molecules in the water.

100.4.2 Oxidation

No information that would support any role for oxidation as an environmental fate process was found in the reviewed literature. Tate and Alexander (1975) have reported that dimethylnitrosamine, which had been dissolved at a concentration of 20 mg/l in samples of water (pH 8.2) collected from Cayuga Lake, New York, persisted without change over an observed period of 3.5 months in the absence of light. The samples were open to the atmosphere and well-stirred, thus ensuring a constant supply of atmospheric oxygen. Under similar conditions, diphenylnitrosamine should be even more resistant to oxidation than dimethylnitrosamine because of the stabilizing influence of the phenyl groups relative to methyl groups.

100.4.3 Hydrolysis

Nitrosamines, in general, are hydrolytically stable at ambient environmental conditions and are reported to be hydrolyzed only at elevated temperatures in strongly acidic solutions (Fieser and Fieser 1956). Tate and Alexander (1975) reported no hydrolytic degradation of dimethylnitrosamine in their Lake Cayuga water samples over the observation period of 3.5

months. Since acid-catalyzed hydrolysis involves protonation of one of the nitrogen atoms, diphenylnitrosamine should be similarly stable to hydrolysis.

100.4.4 Volatilization

Diphenylnitrosamine can be expected to have a low vapor pressure and be highly solvated in water due to hydrogen bonding of water molecules with the nitrosamine group. Moreover, the calculated value of the log octanol/water partition coefficient ($\log P = 2.57$) indicates a definite potential for sorption by organic particulates, thus decreasing further any tendency for this pollutant to volatilize from environmental surface waters.

100.4.5 Sorption

The calculated value of the log octanol/water partition coefficient ($\log P = 2.57$) indicates that diphenylnitrosamine will probably be sorbed by the organic material present in surface waters. No information, however, was found to support this contention.

100.4.6 Bioaccumulation

The calculated value of the log octanol/water partition coefficient ($\log P = 2.57$) indicates a potential for bioaccumulation. No specific information in this regard was found in the reviewed literature.

100.4.7 Biotransformation and Biodegradation

It is difficult to assess the role of biodegradation in the aquatic environment for diphenylnitrosamine. The intestinal microflora of vertebrates are reported to be active in both its synthesis (Ayanaba and Alexander 1973) and degradation (Rowland and Grasso 1975). From these reports it appears that this pollutant is both more easily synthesized and degraded than dialkylnitrosamines. It is not clear, however, whether these observations can be extended to the environment of surface waters.

100.5 Data Summary

Table 100-1 summarizes the aquatic fate data discussed above for diphenylnitrosamine. Photolysis in aqueous solution may be a major degradative process, and sorption by organic material also may have some role in the aquatic fate. Biosynthesis and biodegradation are both more easily accomplished by microorganisms for diphenylnitrosamine than for dialkylnitrosamines.

Table 100-1

Summary of Aquatic Fate of Diphenylnitrosamine

Environmental Process[a]	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Photolysis may be an important fate process.	-	-	Low
Oxidation	Probably not important.	-	-	Low
Hydrolysis	Probably not important.	-	-	Low
Volatilization	Probably not important.	-	-	Low
Sorption	No specific data found; may have significance.	-	-	Low
Bioaccumulation	No specific data found; importance difficult to assess.	-	-	Low
Biotransformation/ Biodegradation	Diphenylnitrosamine is both more easily degraded and synthesized than dialkylnitrosamines.	-	-	Low

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

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Ayanaba, A. and M. Alexander. 1973. Microbial formation of nitrosamines in vitro. Appl. Microbiol. 25(6):862-868.

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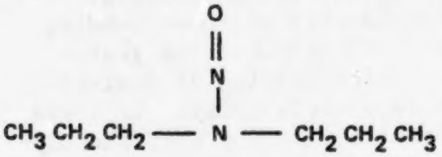
101. DI-n-PROPYLNITROSAMINE

101.1 Statement of Probable Fate

The most probable fate of di-n-propylnitrosamine in the aquatic environment is slow photolytic degradation. Neither volatilization nor sorption processes appear to be major transport mechanisms. Bioaccumulation is probably not important, and, in the event that some of the pollutant should enter into the atmosphere, rapid photodegradation will take place. Di-n-propylnitrosamine exhibits resistance to oxidation, hydrolysis, and microbial degradation.

101.2 Identification

Di-n-propylnitrosamine may be common in the biosphere (Ayanaba and Alexander 1973; Mirvish et al. 1976). The chemical structure of di-n-propylnitrosamine is shown below.



$$CH_3CH_2CH_2-\overset{\substack{O\\ \| \\ N \\ |}}{N}-CH_2CH_2CH_3$$

Di-n-propylnitrosamine

CAS NO. 621-64-7
TSL NO. JL 97000

Alternate Names

N-Nitrosodi-n-propylamine
N-Nitroso-N-propyl-1 propanamine

101.3 Physical Properties

The general physical properties of di-n-propylnitrosamine are listed below.

Molecular weight (Windholz 1976)	130.19
Melting point	No data found
Boiling point at 760 torr (Windholz 1976)	205°C
Vapor pressure	No data found
Solubility in water at 25°C (Mirvish et al. 1976)	9,900 mg/l
Log octanol/water partition coefficient (Calc. by method of Leo et al. 1971 from the data of Mirvish et al. 1976)	1.31

101.4 Summary of Fate Data

101.4.1 Photolysis

The photolytic decomposition of di-n-propylnitrosamine should be essentially similar to the photolytic decomposition of dimethylnitrosamine, since the electronic excitation spectra of both compounds is a general characteristic of dialkylnitrosamines. Dimethylnitrosamine absorbs strongly in the near ultraviolet spectral region at 330 nm with significant absorption occurring up to 400 nm (Polo and Chow 1976). Although dialkylnitrosamines are reported to be relatively stable toward photolysis in neutral aqueous solutions (Chow 1964; Burgess and Lavanish 1964), Polo and Chow (1976) have demonstrated a slow photolytic decomposition of dimethylnitrosamine (initial concentration at 74 mg/l) in aerated distilled water that exhibited zero order kinetics and had a half-life of 79 hours. The observed rate was shown to be dependent on the intensity of irradiation and the design of the apparatus. Chow (1973) has pointed out that the dialkylnitrosamines are photolabile only in dilute acids (pH >1) and that actual protonation of dialkylnitrosamines in strong acids impedes photolysis. Chow's (1973) interpretation of this observation is that hydrogen bonding at the nitroso oxygen atom (rather than protonation) produces the photolabile intermediate; he further speculates that coordination of dialkylnitrosamines with metal cations might also induce photolability. If these speculations should prove to be valid, the possibility exists that photolysis in environmental surface waters could lead to moderately rapid degradation of di-n-propylnitrosamine via hydrogen bonding with humic acids or coordination with metal cations.

In apparent contrast to the results of Chow (1973), MacNaughton and Stauffer (1975) report a half-life of approximately three hours for photolysis of dimethylnitrosamine (200 mg/l) when the solutions are exposed to direct sunlight in covered petri dishes. The solutions, however, were not buffered and, inasmuch as distilled water becomes slightly acidic upon storage due to absorption of atmospheric carbon dioxide, the conditions of this latter photolysis experiment were probably acidic. Indeed, the addition of sodium hydroxide to their experiments greatly reduced the rate of degradation of dimethylnitrosamine in sunlight.

It is uncertain whether volatilization from water will be a significant transport mechanism for di-n-propylnitrosamine. In the event that any dialkylnitrosamine should enter into the atmosphere, it is expected that it will be photolyzed rapidly with a half-life of less than one hour (Hanst et al. 1977; Radding et al. 1977).

101.4.2 Oxidation

No information that would support any role for oxidation as an environmental fate process was found in the reviewed literature. Tate and Alexander (1975) have reported that di-n-propylnitrosamine, which had been dissolved at a concentration of 20 mg/l in samples of water (pH 8.2) collected from Cayuga Lake, New York, persisted without change over an observed period of 3.5 months in the absence of light. The samples were open to the atmosphere and well-stirred, thus ensuring a constant supply of atmospheric oxygen.

101.4.3 Hydrolysis

Nitrosamines, in general, are hydrolytically stable at ambient environmental conditions and are reported to be hydrolyzed only at elevated temperatures in strongly acidic solutions (Fieser and Fieser 1956). Tate and Alexander (1975) reported no hydrolytic degradation of di-n-propylnitrosamine in their samples of Cayuga Lake water over the observation period of 3.5 months.

101.4.4 Volatilization

Di-n-propylnitrosamine has a boiling point of 205°C at atmospheric pressure; it is very soluble in water (9,900 mg/l) and it is apparently highly solvated (Chow 1973). In their spiked lake water samples, Tate and Alexander (1975) observed no loss of di-n-propylnitrosamine due to volatilization or other processes. The water samples were well stirred and maintained at 30°C during the period of observation.

101.4.5 Sorption

No specific information pertaining to sorption phenomena of di-n-propylnitrosamine was found in the reviewed literature. The calculated log octanol/water partition coefficent, however, suggests a moderate potential for sorption by organic matter in the aqueous environment.

101.4.6 Bioaccumulation

No specific information pertaining to bioaccumulation was found in the reviewed literature. Although the calculated log octanol/water partition coefficient indicates a moderate potential for bioaccumulation, this tendency might be offset in vertebrates by the small but not negligible ability of their intestinal microflora to degrade di-n-propylnitrosamine (Rowland and Grasso 1975).

101.4.7 Biotransformation and Biodegradation

Tate and Alexander (1975) have reported that no biodegradation of di-n-propylnitrosamine was observed in their spiked lake water samples over a 3.5 month period, and that a lag of nearly 30 days occurred before its slow disappearance from soil. The nitrosamine appeared to be degraded very slowly in sewage, but it was not affected by the anaerobic organisms of bog sediments collected in a New York wildlife refuge (Tate and Alexander 1976).

101.5 Data Summary

Table 101-1 summarizes the aquatic fate data discussed above for di-n-propylnitrosamine. Photolysis in aqueous solution and, perhaps to a limited extent, in the atmosphere appears to be the major degradative process. At the pollutant levels expected to be found in the aquatic environment, neither volatilization nor sorption processes appear to be major transport or storage mechanisms. Di-n-propylnitrosamine exhibits resistance to microbial degradation in surface waters and, in the absence of photolysis, it could have an appreciable life time.

Table 101-1

Summary of Aquatic Fate of Di-n-propylnitrosamine

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis[a]	Slow photolysis appears to be the only fate process of any consequence.	-	-	Medium
Oxidation	Probably not important.	-	-	Low
Hydrolysis	Probably not important.	-	-	Low
Volatilization	Probably not important.	-	-	Low
Sorption	Probably not important.	-	-	Low
Bioaccumulation	Probably not important.	-	-	Low
Biotransformation/ Biodegradation	Slow degradation is reported to occur in sewage and soil, but this pollutant appears to be resistant to biodegradation in surface waters.	-	-	Medium

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a. The predominant environmental process which is thought to determine the fate of the compound.

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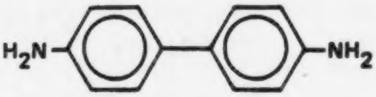
102. BENZIDINE

102.1 Statement of Probable Fate

Benzidine is very rapidly adsorbed by suspended clay particles and is then oxidized by Fe(III), Al(III), or Cu(II) to a blue-colored benzidine radical-cation. From the experimental evidence that is available, it would appear that although both oxidation (by hydroperoxy radical or molecular oxygen) and photolysis can contribute to the environmental fate of benzidine, oxidation by the metal cations of natural waters may be a more rapid process. Benzidine is not bioaccumulated by aquatic organisms, and it is apparently not easily degraded by the microorganisms in sewage plant sludge. Benzidine itself does not appear to be a persistent constituent of natural surface waters, but very little is known about the characteristics of its degradation products.

102.2 Identification

Benzidine has been detected in industrial effluents (Shackelford and Keith 1976). The chemical structure of benzidine is shown below.



Benzidine

CAS NO. 92-87-5
TSL NO. DC 96250

Alternate Names

4,4'-Diaminobiphenyl
4,4'-Biphenyldiamine
(1,1'-Biphenyl)-4,4'-diamine

102.3 Physical Properties

The general physical properties of benzidine are as follows.

Molecular weight (Verschueren 1977)	184.23
Melting point (Verschueren 1977)	129°C
Boiling point at 760 torr (Verschueren 1977)	402°C
Vapor pressure	No data found

Solubility in water at 12°C (Verschueren 1977)	400 mg/l
Log octanol/water partition coefficient (Radding et al. 1977)	1.81

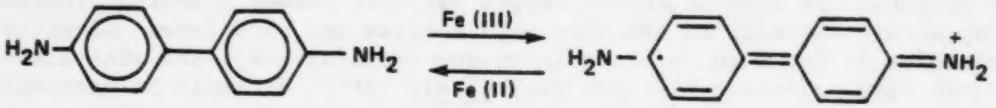
102.4 Summary of Fate Data

102.4.1 Photolysis

The absorption maximum for benzidine in aqueous ethanol is 287 nm with significant absorption in the ultraviolet region extending to 340 nm (Bilbo and Wyman 1953). The capability of benzidine to absorb electromagnetic energy in the near ultraviolet region makes photolysis a distinct possibility. Nonetheless, no information was found demonstrating that direct photolysis was an aquatic fate. Moreover, Howard and Saxena (1976), in commenting on the reports of the Synthetic Organic Chemical Manufacturer's Association (SOCMA) Benzidine Task Force, point out that the reported photolysis experiments were carried out in aerated water, and that the observed rate of disappearance of benzidine was the same as (or slower than) that which had been observed in the absence of light. There is, however, indirect evidence that benzidine can act as a photosensitizer. Specifically, N,N,N',N'-tetramethylbenzidine is excited to a triplet state when irradiated at 347 nm in organic solvents (Alkaitis and Grätzel 1976), but this triplet state is rapidly quenched by oxygen ($k=2.8 \times 10^{10}$ l. mole^{-1}sec^{-1}). A competing photochemical reaction that occurs during triplet formation is photoionization to form a tetramethylbenzidine radical-cation. Assuming that benzidine itself will undergo photoionization in a similar manner, the resulting benzidine radical-cation, which is known to be formed rapidly via oxidation in the presence of montmorillonite (Lahav and Raziel 1971) could presumably undergo further photolysis since it absorbs visible radiation strongly.

102.4.2 Oxidation

Benzidine is very rapidly oxidized by iron(III) and several other naturally occurring cations (Lahav and Raziel 1971) which are found in environmental waters as solvated cations, complexes of fulvic acids, and as parts of the structure of microcrystalline clays (Gould 1968). When benzidine is brought into contact with montmorillonite, there is formed an intensely blue-colored complex due to the oxidation of benzidine to benzidine radical-cation by the iron(III) in the clay structure (Tennakoon et al. 1974).



Although this reaction is readily reversible, Fe(II) in aerated environmental waters would be quickly reoxidized to Fe(III) due to the presence of dissolved oxygen or other electron acceptors. Tennakoon et al. (1974) have presented evidence that this benzidine radical-cation can become intercalated between the layers of the clay structure.

The formation of benzidine radical-cation from the oxidation of benzidine by metal cations may explain the observations of the SOCMA Benzidine Task Force as reported by Howard and Saxena (1976). The degradation of benzidine in lake water (obtained from a Buffalo, New York pumping station) was measured in chlorinated water and aerated water (both stirred and undisturbed) in the absence of light. The data were subjected to statistical analysis and showed no significant differences under the different conditions. By plotting the reaction rates, it was concluded that the degradation of benzidine was probably first order with a rate constant of 0.175 $hour^{-1}$ ($t_{1/2}$ = 4 hours). Since all of these experiments were conducted with the same sample of lake water, the rate probably was governed by the concentration and sorption state of the naturally occurring metal cations in the water. The reduced cations would have been reoxidized by either chlorine or oxygen.

Indirect photolysis of benzidine, involving reaction with hydroperoxy radical or excited oxygen, may be an important fate process for this pollutant. There are two competing photochemical pathways that ensue during irradiation of N,N,N',N'-tetramethylbenzidine: triplet formation and photoionization (Alkaitis and Grätzel 1976). The triplet is rapidly quenched by oxygen ($k = 2.8 \times 10^{10}$ l $mole^{-1}sec^{-1}$) and photoionization produces a tetramethylbenzidine radical-cation and a solvated electron. By inference, similar photochemical pathways may exist for benzidine. No provisions were made to deoxygenate the water that was used for the photolysis experiments carried out by SOCMA, but it was stated to be deionized (Howard and Saxena 1976), thus precluding the participation of metal cations in this latter set of experiments. Inasmuch as solvated electrons react with water to form hydrogen atoms which in turn can form hydroperoxy radicals with oxygen, benzidine could have been attacked by excited oxygen or hydroperoxy radicals. In the presence of sufficient oxygen, it can also be hypothesized that molecular oxygen may have formed a charge-transfer complex with benzidine, and that this complex was photolyzed directly. Benzidine is known to form stable charge-transfer complexes with electronegative molecules (Van der Hoek et al. 1960). It would be meaningless to attempt derivation of definitive reaction rates from the SOCMA study because the rate of degradation was characteristic of the water samples themselves, and it is evident that several reactions were occurring concurrently.

It is somewhat difficult to speculate on the environmental fate of benzidine radical-cation. Tennakoon et al. (1974) seem to indicate that it has a certain degree of stability when it is intercalated between the layers of the clay structure of montmorillonite; however, molecules that have a semiquinone-like structure are in general easily oxidized. From the experimental evidence that is available, it would appear that, although both oxidation and photolysis can contribute to the environmental fate of benzidine, oxidation by the metal cations of natural waters may be the most rapid process. At the concentrations of benzidine expected to be found in environmental waters, this oxidation by metal cations would not be a catalytic step in the oxidation of benzidine by oxygen but instead would be competitive with direct reaction with oxygen.

102.4.3 Hydrolysis

There are no data to suggest that hydrolysis of benzidine is an environmentally significant process. The covalent bond of a substituent attached to an aromatic ring is usually resistant to hydrolysis because of the high negative charge-density of the aromatic nucleus. Benzidine, as well as many other aromatic amines, forms bisulfite addition complexes in aqueous bisulfite solutions (Drake 1942). During the aqueous decomposition of these complexes, the amino group is replaced by a hydroxy group.

102.4.4 Volatilization

Since benzidine has a boiling point of 402°C (Verschueren 1977) and a moderate aqueous solubility, volatilization from water at ambient environmental temperatures is not expected to be a significant transport process. Data, however, are lacking. Although benzidine can be protonated to form a cation which cannot volatilize from water, the pK_a values of the diprotonated and monoprotonated conjugate acids of benzidine have been reported as 3.3 and 4.5, respectively (Korenman and Nikolaev 1974). Therefore, dissolved benzidine will be present almost entirely in the form of a free base in naturally occurring waters.

102.4.5 Sorption

The moderate value of the octanol/water partition coefficient indicated by log P=1.81 (Radding et al. 1977) suggests little potential for sorption by organic particulates. Adsorption by clay minerals, on the other hand, is so rapid that great difficulty has been encountered in measuring the kinetics of this process (Lahav and Raziel 1971). Sorption to clay minerals and metal cation complexes may be the most important transport process for this pollutant in the aquatic environment. Intercalation of the benzidine radical-cation into the clay structure of montmorillonite (Tennakoon et al. 1974) may increase its stability in environmental waters. Depending upon whether or not these clay particles then become part of the bed sediment, benzidine radical-cation could be broadly transported in surface water systems without being detected by most methods of chemical analysis for benzidine.

102.4.6 Bioaccumulation

The log octanol/water partition coefficient indicates that benzidine should not be bioaccumulated significantly in the aquatic environment. This supposition seems to be supported by data obtained by Kellner et al. (1973) who found almost no radioactivity in the tissues of rats, dogs, and monkeys seven days after intravenous administration of radiolabeled benzidine. Although the urine of these animals contained benzidine, most of the radioactivity was associated with metabolites. Substantiation more germane to the problem of water pollution has been given by Lu et al. (1977) who found that, although radiolabeled benzidine was taken up by the organisms of their aquatic ecosystem, it was not bioaccumulated and it remained in equilibrium with the benzidine dissolved in the water.

102.4.7 Biotransformation and Biodegradation

Kellner et al. (1973) studied the kinetics and distribution pattern of benzidine in rats, dogs, and monkeys. In the monkey 99 percent of the injected benzidine was excreted as metabolites in the urine, whereas only 0.1 percent was excreted as unchanged benzidine. Detoxification apparently proceeds via acetylation of the amino groups.

The SOCMA Benzidine Task Force has examined the biological degradation of benzidine under the conditions that would be met in a sewage treatment plant (Howard and Saxena 1976). At concentrations of 60 to 120 mg/l, benzidine inhibited the oxygen uptake of sludge that had been acclimated to aniline; at concentrations of 40 to 80 mg/l, the oxygen uptake of unacclimated sludge was also inhibited. At µg/l concentrations, however, benzidine was partially degraded. Baird et al. (1977) have reported the biodegradation of benzidine by activated sludge at several different concentrations all of which were over 100 mg/l, and they also stated that acclimation appeared to be unnecessary. In contrast, Tabak and Barth (1978), using a flow reactor designed to simulate sludge-treatment operations, found that six weeks were required for acclimation of activated sludge exposed to 5 mg/l of the pollutant. At benzidine concentrations of 10 mg/l and higher, the same flow reactor failed to achieve acclimation. The extent of microbial degradation of benzidine in natural waters is unknown.

102.4.8 Other Reactions

Jenkins et al. (1978) report that benzidine does not undergo chlorination of the aromatic rings under the conditions of disinfection in a water treatment plant. Treatment of an aqueous solution of benzidine with chlorine apparently produces an oxidized intermediate which forms a high molecular weight, dark purple precipitate. Analysis of the precipitate and the supernatant liquid failed to disclose the presence of any chlorinated aromatic compounds.

102.5 Data Summary

The most striking chemical feature of benzidine is the rapidity with which it reacts with suspended microcrystalline clays to form a blue complex in which the benzidine is present as benzidine radical-cation. Photolysis, direct oxidation with molecular oxygen, and indirect photolysis may all contribute to the degradation of benzidine but the most rapid process of environmental consequence is probably oxidation by naturally occurring metal cations.

Table 102-1

Summary of Aquatic Fate of Benzidine

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Photolysis probably makes a direct contribution to the aquatic fate of benzidine and its degradation products.	-	-	Medium
Oxidation[a]	Although photooxidation and direct interaction with molecular oxygen or hydroperoxy radical probably contribute to the fate of benzidine, the most rapid aquatic redox process appears to be oxidation by naturally occurring metal cations.	-	4 hours[b]	High
Hydrolysis	Probably not important.	-	-	High
Volatilization	Probably not important.	-	-	High
Sorption	Adsorption by suspended microcrystalline clays may be the most rapid process in the environment.	-	-	High
Bioaccumulation	Does not appear to be important in aquatic organisms.	-	-	Medium
Biotransformation/ Biodegradation	Biodegradation may contribute slightly to the degradation of benzidine during sewage plant treatment. No information was found about environmental degradation.	-	-	Medium

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a. The predominant environmental process which is thought to determine the fate of the compound.

b. This was the half-life that was observed for benzidine in a sample of water taken from a Buffalo, N.Y. pumping station. The rate of degradation remained the same in aerated, chlorinated or untreated water (Howard and Saxena 1976).

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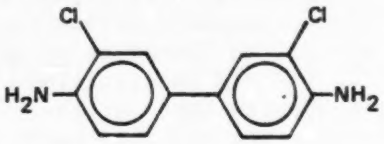
103. 3,3'-DICHLOROBENZIDINE

103.1 Statement of Probable Fate

The most probable fate of 3,3'-dichlorobenzidine in natural surface waters is adsorption by particulates and sediment. Most of the ultimate degradation occurs within the sediment via chemical processes. In addition, photolytic dechlorination is very rapid in shallow water. The products of photolysis are benzidine, 3-chlorobenzidine, and several unidentified acidic materials. Fish bioconcentrate this pollutant but biodegradation as an environmental or sewage-plant process appears to be inoperative. Volatilization from surface waters is not significant, and 3,3'-dichlorobenzidine in natural water systems is transported both as a solute and as an adsorbate on suspended particulates.

103.2 Identification

The chemical structure of 3,3'-dichlorobenzidine is shown below.



3,3'-Dichlorobenzidine

CAS NO. 91-94-1
TSL NO. DD 05250

Alternate Names

3,3'-Dichloro-4,4'-diamino-(1,1'-biphenyl)

103.3 Physical Properties

The available physical properties of 3,3'-dichlorobenzidine are given below.

Molecular weight (Windholz 1976)	253.12
Melting point (Windholz 1976)	132°C
Boiling point	No data found*

Vapor pressure	No data found
Solubility in water at 22°C (pH 7) (Banerjee *et al*. 1978)	4 mg/l**
Log octanol/water partition coefficient (Calc. by method of Leo *et al*. 1971)	3.02

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*The boiling point for unsubstituted benzidine at 760 torr is 402°C (Verschueren 1977).

**Solubility given as the dihydrochloride.

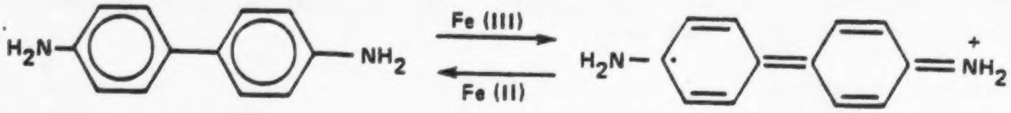
103.4 Summary of Fate Data

103.4.1 Photolysis

The absorption maximum for 3,3'-dichlorobenzidine in aqueous ethanol is 290 nm with significant absorption in the ultraviolet region extending to 340 nm (Bilbo and Wyman 1953). In dilute aqueous solution the absorption maxima have been observed at 282 nm and 211 nm (Banerjee *et al*. 1978; Sikka *et al*. 1978). 3,3'-Dichlorobenzidine (10^{-5} M in distilled water), when exposed to noonday summer sunlight in quartz tubes at the latitude of Syracuse, New York, is degraded rapidly. The reported half-life under these conditions is 90 seconds (Sikka *et al*. 1978). A significant but variable portion is converted to 3-chlorobenzidine which upon prolonged irradiation for several hours is further dechlorinated to benzidine (Banerjee *et al*. 1978; Sikka *et al*. 1978). Analysis of the irradiated solutions by thin-layer chromatography disclosed the presence of small amounts of at least five brightly colored acidic substances. Irradiation of a more concentrated solution with a 450 W medium-pressure mercury lamp equipped with a Pyrex filter confirmed the stepwise dechlorination of 3,3'-dichlorobenzidine but also resulted in the formation of reddish-brown insoluble material deposited on the walls of the photoreactor. Short-lived, green transient intermediates were observed when the irradiation was carried out in acidic solutions (Banerjee *et al*. 1978). Banerjee *et al*. (1978) postulate that, since the chlorine substituent was not being replaced by a hydroxy group derived from the aqueous solvent, the chlorine substituent is probably being removed as a chlorine atom or chlorine cation rather than as a chloride anion. Thus, the green transient intermediate should be an oxidation product of 3,3'-dichlorobenzidine. In support of this postulate, when a drop of chlorine-water was added to a dilute aqueous solution of 3,3'-dichlorobenzidine, the same (or similar) green transient was observed. One possible explanation for these latter observations of Banerjee et al. (1978) is that photolysis of 3,3'-dichlorobenzidine could produce a radical-cation similar to that produced by the photolysis of N,N,N',N'-tetramethylbenzidine (Alkaitis and Grätzel 1976) or the metal-cation oxidation of unsubstituted benzidine (Lahav and Raziel 1971; Tennakoon et al. 1974). If 3,3'-dichlorobenzidine itself can undergo photoionization, the resulting radical-cation may be the green transient intermediate that subsequently loses a neutral or positive chlorine atom.

103.4.2 Oxidation

Unsubstituted benzidine is very rapidly oxidized by iron(III) and several other naturally occurring cations (Lahav and Raziel 1971) which can be found in environmental waters as solvated cations, complexes of humic acids, and as parts of the structure of microcrystalline clays (Gould 1968). When unsubstituted benzidine is brought into contact with montmorillonite, there is formed an intensely blue-colored complex due to the oxidation of benzidine to benzidine radical-cation by the iron(III) in the clay structure (Tennakoon et al. 1974).



Although this reaction is readily reversible, Fe(II) in aerated environmental waters would be quickly reoxidized to Fe(III) due to the presence of dissolved oxygen or other electron acceptors. Whether or not 3,3'-dichlorobenzidine will be oxidized rapidly in a similar fashion depends upon its ionization potential in relation to the ionization potential of benzidine itself. Due to the two chlorine substituents on the aromatic rings, 3,3'-dichlorobenzidine will have a lesser tendency to lose an electron than unsubstituted benzidine. The oxidation of 3,3'-dichlorobenzidine by metal cations and other environmental electron acceptors in natural sediments and sewage sludge may explain in part the poor recoveries of this pollutant described by Sikka et al. (1978) in experiments with these natural materials.

103.4.3 Hydrolysis

There are no data to suggest that hydrolysis of 3,3'-dichlorobenzidine is an environmentally significant process. The covalent bond of a substituent attached to an aromatic ring is usually resistant to hydrolysis because of the high negative charge-density of the aromatic nucleus. The only conceivable conditions under which this pollutant might be subject to hydrolysis in the aqueous environment are those which could occur in the vicinity of a paper mill or coal mine. Unsubstituted benzidine, as well as many other aromatic amines, forms bisulfite addition complexes in aqueous bisulfite solutions (Drake 1942). During the aqueous decomposition of these complexes, the amino group is replaced by a hydroxy group.

103.4.4 Volatilization

The fact that unsubstituted benzidine has a boiling point of 402°C (Verschueren 1977) indicates that volatilization from water at ambient environmental temperatures is probably not a significant transport process. The vapor pressure of 3,3'-dichlorobenzidine will be considerably lower at ambient environmental conditions than what will obtain for unsubstituted benzidine. Although benzidine can be protonated to form a cation which cannot volatilize from water, the pK_a values of the diprotonated and monoprotonated conjugate acids of benzidine have been reported as 3.3 and 4.5 (Korenman and Nikolaev 1974). Therefore, dissolved benzidine will be present almost entirely in the form of a free base in naturally occurring waters. Similarly, 3,3'-dichlorobenzidine can be expected to be present mostly in the form of a free base.

103.4.5 Sorption

The value of the octanol/water partition coefficient for 3,3'-dichlorobenzidine corresponding to log P=3.02 (Leo et al. 1971) indicates considerable tendency for sorption by organic particulates. Moreover, adsorption by clay minerals of unsubstituted benzidine is so rapid that great difficulty has been encountered in measuring the kinetics of this process (Lahav and Raziel 1971). Sorption to clay minerals and metal cation complexes is probably the most rapid process for unsubstituted benzidine in the aquatic environment.

Sorption of 3,3'-dichlorobenzidine by several sediments obtained from natural surface waters was both rapid and to a great extent irreversible (Sikka et al. 1978). To determine sorption, an aqueous solution of 2 mg/l of 3,3'-dichlorobenzidine was mixed with a sediment to give a water: sediment ratio of 100:1. With all samples, sorption was approximately 50% complete within 30 minutes and more than 90% complete after 5 hours. Neither rate of sorption nor ease of desorption could be correlated by Sikka et al. (1978) with the organic content of the sediment. After 24 hours of exposure of the sediments to 3,3'-dichlorobenzidine, aqueous solutions of 5 N NH_4Cl, 1 N HCl, and 1 N NaOH could only extract 2, 9, and 31%, respectively, of the sorbed pollutant. Methanol extracted 36%, and a second portion of methanol extracted only an additional 4%. Exposure of the sediments to the pollutant for seven days decreased the amount of 3,3'-dichlorobenzidine extracted by all of the above extractants by about 50%. Sikka et al. (1978) did not consider the possibility of sorption by clay; and although the clay content was listed for two of the sediments as <1%, that percent of clay would be the equivalent of zero to 99 mg/l in each experimental container. If 3,3'-dichlorobenzidine behaves similarly to benzidine in the presence of clay, the 2 mg/l of pollutant could have been rapidly sorbed, partially converted to a radical-cation, and intercalated within the clay structure. This type of organic-inorganic interaction may explain the observed data from the sorption experiments of Sikka et al. (1978) and may also account for the environmental fate of any 3,3'-dichlorobenzidine that is not photolyzed near the air-water surface.

103.4.6 Bioaccumulation

The calculated log octanol/water partition coefficient (log P=3.02) indicates that 3,3'-dichlorobenzidine has the potential to be bioaccumulated in the aquatic environment. This supposition is supported by the results of experiments conducted by Sikka et al. (1978). 3,3'-Dichlorobenzidine is bioconcentrated by fish to a significant degree directly from contaminated water. In the experiment represented by Table 103-1, bluegills were exposed to the pollutant at a concentration (given as the dihydrochloride) of 2 ppm. Uptake was very rapid, and residues in the fish increased throughout the 48 hours of exposure. Initial bioconcentration occurred predominantly in the non-edible portions. After 24 hours, however, bioconcentration in the edible portion increased markedly. By 48 hours, the fish exhibited toxic symptoms, and within several hours the entire test group died.

Because of the toxicity encountered in the former experiment, a second group of bluegills was exposed to 3,3'-dichlorobenzidine at a concentration of 0.5 ppm of the dihydrochloride (Table 103-2; Sikka et al. 1978). After 72 hours, however, only about 10% of the exposed fish responded to stimuli. Between 96 and 120 hours, approximately one-half of the remaining test group died, and the survivors exhibited extreme toxic symptoms. As in the previous experiment, pollutant residues in the head and viscera initially increased faster than in the edible portion. The surviving fish were placed in fresh water which was flowing at a rate to give 12 complete renewals of fresh water per 24 hours. The depuration of 3,3'-dichlorobenzidine is shown in Table 103-3. Although the rate of elimination was initially rapid, the levels of 3,3'-dichlorobenzidine became virtually constant after 120 hours.

Table 103-1

^{14}C Distribution in Bluegills Exposed to 2.0 ppm ^{14}C-DCB·2HCl

	ppm-DCB Equivalent[a]		
Exposure Time (hours)	Edible Flesh	Head and Viscera	Whole Fish
3	92.9 ± 1.9	151.1 ± 2.3	119.2 ± 1.8
6	83.6 ± 3.5	179.1 ± 13.0	123.1 ± 7.3
24	75.6 ± 2.2	368.7 ± 9.5	187.0 ± 3.8
48	192.5 ± 4.9	358.8 ± 6.1	265.3 ± 7.3

a. The values are the average of two experiments, with three fish per experiment sampled at each exposure interval. Non-extractable ^{14}C residues were less than 0.5% of total ^{14}C (<0.1 ppm). From Sikka *et al*. (1978).

Table 103-2

^{14}C Distribution in Bluegills Exposed to 0.5 ppm ^{14}C-DCB·2HCl

	ppm-DCB Equivalent[a]		
Exposure Time (hours)	Edible Flesh	Head and Viscera	Whole Fish
24	20.5 ± 1.3	98.2 ± 6.4	59.4 ± 2.8
48	39.0 ± 0.3	193.5 ± 13.4	109.7 ± 4.1
72	118.5 ± 6.6	207.1 ± 27.6	164.1 ± 13.7
96	98.3 ± 7.1	212.6 ± 15.3	151.3 ± 10.3
120	213.2 ± 9.4	372.4 ± 29.6	277.0 ± 14.8

a. Values are the average of two experiments, with two fish per experiment sampled at each exposure interval. Non-extractable ^{14}C residues were less than 0.5% of total ^{14}C (<0.1 ppm). From Sikka *et al*. (1978).

Table 103-3

Elimination of ^{14}C From Bluegills Exposed to 0.5 ppm ^{14}C-DCB·2HCl

Depuration Time (hrs.)	Percent of Initial ^{14}C Remaining[a]		
	Edible Flesh	Head and Viscera	Whole Fish
24	-	-	56[b]
120	5.2 ± 0.3	14.4 ± 0.1	11.6 ± 0.2
240	2.6 ± 0.1	19.7 ± 0.1	13.3 ± 0.1

a. Initial ^{14}C residues were 213.2 ppm, 372.4 ppm, and 277.0 ppm for edible flesh, head and viscera, and whole fish, respectively (average of 2 experiments). Depuration data are the average of duplicate experiments (4 fish per experiment).

b. Calculated from the ^{14}C in depuration water over the first 24 hours of the experiment. From Sikka et al. (1978).

103.4.7 Biotransformation and Biodegradation

According to the experiments of Sikka et al. (1978), 3,3'-dichlorobenzidine was not metabolized by microorganisms over a four-week period in samples of water taken from Oneida Lake (New York) and Jamesville Reservoir (New York). The water from the reservoir had 5 x 10^6 microbial cells per milliliter. The observed small decrease of the pollutant in the water was found to be due to adsorption by suspended sediment. Similarly, activated sludge did not degrade the pollutant and attempts to produce an acclimated sludge through weekly subculturing were unsuccessful (Sikka et al. 1978). Bluegills that had been exposed to 3,3'-dichlorobenzidine were shown to be capable of converting a small part of the pollutant to a water-soluble, polar derivative which was, however, hydrolytically unstable and easily reverted to 3,3'-dichlorobenzidine (Sikka et al. 1978). Kellner et al. (1973) studied the kinetics and distribution pattern of 3,3'-dichlorobenzidine in rats, dogs, and monkeys. Most of the injected 3,3'-dichlorobenzidine was excreted unchanged in the feces by these terrestrial mammals.

103.5 Data Summary

Table 103-4 summarizes the aquatic fate data for 3,3'-dichlorobenzidine. Although photolysis of a dilute solution of the pollutant exposed to direct sunlight is very rapid ($t_{1/2}$ ~ 90 sec), the predominant fate probably is sorption by sediments and suspended organic and inorganic particulates. The irreversibility of this sorption process probably makes degradation within the sediments this pollutant's principal aquatic fate. Photolytic dechlorination produces 3-chlorobenzidine and benzidine itself. In addition, several unidentified acidic materials are formed photolytically. 3,3'-Dichlorobenzidine is bioconcentrated by fish but biodegradation appears to be inoperative as an environmental or sewage-plant process. Hydrolysis and volatilization are similarly insignificant. 3,3'-Dichlorobenzidine is probably transported within the water column both as a solute and as an adsorbate. Its observed behavior in natural water samples suggests that this pollutant would soon become part of the bed sediment.

Table 103-4

Summary of Aquatic Fate of 3,3'-Dichlorobenzidine

Environmental Process	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Photolysis probably makes a direct contribution to the aquatic fate of 3,3'- dichlorobenzidine and its degradation products.	-	~90 sec [a]	High
Oxidation	Oxidation by naturally occurring metal cations may contribute to the degradation of this pollutant in sediments.	-	-	Medium
Hydrolysis	Probably not important.	-	-	Low
Volatilization	Probably not important.	-	-	Low
Sorption[c]	Adsorption by suspended microcrystalline clays may constitute the most important fate process in the aquatic environment.	-	~30 min [b]	High
Bioaccumulation	Bioconcentrated in fish at subtoxic levels.	-	-	High
Biotransformation/ Biodegradation	Pollutant does not appear to be degraded by aquatic microorganisms, activated sludge, fish, or terrestrial mammals.			High

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[a] Half-life of 3,3'-dichlorobenzidine in a dilute aqueous solution exposed to the noonday sun during the summer at Syracuse, New York (Sikka et al. 1978).

[b] Rate of adsorption for several sediments of varying composition at 100:1 water:sediment ratios. (Sikka et al. 1978).

[c] The predominant environmental process which is thought to determine the fate of the compound.

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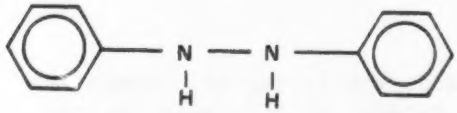
104. 1,2-DIPHENYLHYDRAZINE (HYDRAZOBENZENE)

104.1 Statement of Probable Fate

1,2-Diphenylhydrazine is in rapid redox equilibrium with azobenzene. Since this reaction is easily reversible, it does not in itself serve as an environmental fate but it may influence the properties of sorption and volatilization as well as the degradative pathway. In aerated waters azobenzene should predominate, but if the conditions of the water body were to become reducing, the azobenzene will revert to 1,2-diphenylhydrazine. Photoreduction or biodegradation of this pollutant can produce aniline which would then eventually be further degraded. Reduction to aniline may be the only pathway to mineralization under the environmental conditions of ambient surface waters. Sorption onto particulates probably provides the main transport mechanism for this pollutant, and, in the absence of a reasonably rapid biodegradation or photoreduction to aniline, sorption by the bed sediment as both 1,2-diphenylhydrazine and azobenzene could be the pollutant's short-term environmental fate.

104.2 Identification

1,2-Diphenylhydrazine is in easily reversible redox equilibrium with azobenzene (Griffiths 1972; Rao and Hayon 1976). The relative concentrations of the two compounds that will be present at any time depends upon the oxidation potential of the sample of water. In well aerated water the more oxidized compound, azobenzene, will predominate (Blackadder and Hinshelwood 1957). 1,2-Diphenylhydrazine has been detected in finished drinking water and azobenzene has been found in an industrial effluent (Shackelford and Keith 1976). The chemical structure of 1,2-diphenylhydrazine is shown below.



1,2-Diphenylhydrazine

CAS NO. 122-66-7
TSL NO. MW 26250

Alternate Names

Hydrazobenzene
N,N'-Bianiline

104.3 Physical Properties

The general physical properties of 1,2-diphenylhydrazine are given below. The footnotes provide properties of azobenzene.

Molecular weight (Weast 1977)	184.24
Melting point (Weast 1977)	131°C
Boiling point at 760 torr	No data found*
Vapor pressure	No data found**
Solubility in water	No data found***
Log octanol/water partition coefficient (Calc. by method of Leo *et al*. 1971)	3.03****

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*The boiling point of azobenzene has been reported as 293°C (IARC 1975). 1,2-Diphenylhydrazine will be rapidly converted to azobenzene at the air-water interface.

**The vapor pressure of azobenzene is given as 1 torr at 103°C (IARC 1975).

***The solubility of azobenzene in water at 20°C has been determined to be 0.252 mg/1 (Takagishi *et al*. 1968).

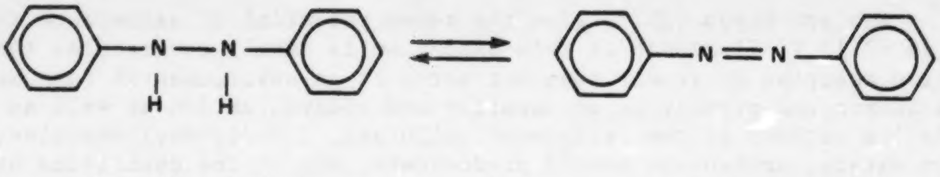
****The log octanol/water partition coefficient of azobenzene has been determined to be 3.82 (Fujita *et al*. 1964).

104.4 Summary of Fate Data

104.4.1 Photolysis

Although 1,2-diphenylhydrazine absorbs electromagnetic radiation up to 310 nm, the ultraviolet photolysis of aerated solutions in organic solvents yields only azobenzene (Shizuka *et al*. 1970), while under a nitrogen atmosphere azobenzene and aniline are the observed products (Hashimoto *et al*. 1968). The latter reaction may have degradative significance if the 1,2-diphenylhydrazine is sorbed onto organic particulates.

1,2-Diphenylhydrazine is rapidly oxidized to azobenzene in aerated solutions (Blackadder and Hinshelwood 1957; Rao and Hayon 1976) and in solutions that contain such environmentally common cations as Cu(II) and Fe(III) (Blackadder and Hinshelwood 1957). Inasmuch as this oxidation is easily reversible (Griffiths 1972; Rao and Hayon 1976), the oxidation



reaction in itself does not serve as an environmental fate but it has the potential of providing a route to destruction via photochemical reactions of azobenzene. The lowest energy-transition of azobenzene occurs in the visible spectral region at 440 nm and 430 nm for the trans and cis forms, respectively (Griffiths 1972). The resulting singlet states are hypothesized by Griffiths (1972) as those being most likely to be involved in solution-phase photochemical reactions. The three photochemical reactions of azobenzene that have been described in the literature are the rapidly reversible cis-trans isomerization, cyclodehydrogenation, and reduction to 1,2-diphenylhydrazine (Griffiths 1972). Of these three, only reduction to 1,2-diphenylhydrazine could have any possible relevance with regard to environmental pollutant degradation. Cyclodehydrogenation requires either a concentrated mineral acid medium or an anhydrous solvent that contains electron-accepting Lewis acids (Joshua and Pillai 1974). Photoreduction in organic solvents results in the formation of 1,2-diphenylhydrazine and a small amount of aniline (Griffiths 1972). Since a hydrogen donor must be present, photoreduction could only take place in surface waters if the azobenzene were sorbed by organic particulates. Several photochemically produced hydrogen donors can themselves reduce azobenzene. The most relevant example with respect to environmental water chemistry is the reduction brought about by chlorophyll and its derivatives (Livingston and Pariser 1948). Azobenzene could in this fashion be reduced after being sorbed by aquatic plants or particulates derived from them. The collapse of algal blooms, for example, produces reducing conditions plus chlorophyll-containing particulates.

104.4.2 Oxidation

1,2-Diphenylhydrazine is oxidized by molecular oxygen in aerated solutions (Blackadder and Hinshelwood 1957). The rate is pH-dependent in a well aerated solution and is catalyzed by the presence of Cu(II) and Fe(III) cations. Blackadder and Hinshelwood (1957) report a first order rate constant equal to 2×10^{-3} sec^{-1} for the uncatalyzed reaction at pH 10, and 1×10^{-2} sec^{-1} for the copper-catalyzed reaction at the same pH. The corresponding half-lives with respect to oxidation are 5.78 min. and 1.16 min., respectively. At dilute concentrations of 1,2-diphenylhydrazine, the rate of oxidation by 10^{-5} M cupric ion remained the same in the presence or absence of oxygen. No data were given from which a rate constant at pH 7 could be calculated, although it was reported that the reaction proceeded at an observable rate even in acidic solutions.

Rao and Hayon (1976) give the redox potential of azobenzene in water as -0.12 V. Inasmuch as this oxidation is easily reversible, the oxidation reaction in itself does not serve as an environmental fate but it may influence the properties of sorption and volatilization as well as the degradative pathway of the designated pollutant, 1,2-diphenylhydrazine. In aerated waters, azobenzene should predominate, but if the conditions of the water body should become reducing, e.g., in the presence of sulfide or hydrosulfide (Hashimoto and Sunamoto 1966), the azobenzene will revert to 1,2-diphenylhydrazine. No information indicating that further oxidation of azobenzene would occur at ambient environmental conditions was found.

104.4.3 Hydrolysis

There are no data to suggest that hydrolysis of 1,2-diphenyl-hydrazine is an environmentally significant process. The covalent bond of a substituent attached to an aromatic ring is usually resistant to hydrolysis because of the high negative charge-density of the aromatic nucleus. Conditions under which 1,2-diphenylhydrazine might be subject to hydrolysis in the aqueous environment include those which could obtain in the bisulfite wastes of a paper mill or coal mine. 1,2-Diphenylhydrazine, as well as many other aromatic hydrazines and amines, forms bisulfite addition complexes in aqueous bisulfite solutions (Drake 1942). During the aqueous decomposition of these complexes, the hydrazine moiety is replaced by a hydroxy group, resulting in the formation of phenol.

104.4.4 Volatilization

At the air-water interface the pollutant, 1,2-diphenylhydrazine, will be present predominantly as azobenzene. Therefore, an assessment of the volatility of this pollutant from surface waters should take into consideration the vapor pressure, solubility, and sorption of azobenzene rather than 1,2-diphenylhydrazine. The vapor pressure of azobenzene at 103°C is given as 1 torr (IARC 1975) and the solubility of azobenzene in water at 20°C has been determined by Takagishi et al. (1968) to be 2.512×10^{-8} mole fraction, corresponding to 0.252 mg/l. In addition, the log octanol/water partition coefficient is reported by Fujita et al. (1964) as 3.82, indicating a definite preference for organic material, and azobenzene is also well known to be strongly adsorbed by silicate minerals (Sato 1956). From these data it can be inferred that azobenzene will be very strongly sorbed by the particulates of natural surface waters and probably will exhibit very little tendency to be transported by volatilization from the aqueous environment.

104.4.5 Sorption

The log octanol/water partition coefficient of 3.03 for 1,2-diphenylhydrazine, calculated by the method of Leo et al. (1971), and the value for azobenzene of 3.82, reported by Fujita et al. (1964), indicate a definite partitioning preference for organic material. Additionally, azobenzene is well known to be strongly adsorbed by silicate minerals (Sato 1956; Zubareva et al. 1974). Sorption onto particulates is probably the main transport process for this pollutant and, in the absence of significant biodegradation or photoreduction to aniline, sorption by the bed sediment as both 1,2-diphenylhydrazine and azobenzene may be its environmental fate.

104.4.6 Bioaccumulation

The log octanol/water partition coefficient for 1,2-diphenylhydrazine of 3.03, calculated by the method of Leo et al. (1971), and the value of log P for azobenzene of 3.82, reported by Fujita et al. (1964), indicate a definite potential for bioaccumulation. There was, however, no biological information found in the literature to support this contention.

104.4.7 Biotransformation and Biodegradation

Rats, which had been given 1,2-diphenylhydrazine, excreted in the urine unchanged 1,2-diphenylhydrazine, benzidine, aniline, para-aminophenol, and ortho-aminophenol (Dutkiewicz and Szymanska 1973). Azobenzene was reported to be similarly detoxified to aniline and benzidine (Elson and Warren 1944). The only microbiological study of biotransformation that was found reported that fresh baker's yeast reduced azobenzene to a compound tentatively identified as 1,2-diphenylhydrazine (Mecke and Schmähl 1957).

104.4.8 Other Reactions

1,2-Diphenylhydrazine rearranges intramolecularly to benzidine in aqueous acid. Although the concentration of aqueous acid that is necessary for this reaction is unlikely to be found in ambient surface waters, this rearrangement can proceed easily in the presence of anionic micelles such as would be formed from commercial laundry detergents. Bunton and Rubin (1975) report that the maximum rate constant for the benzidine rearrangement in 1 mM aqueous HCl (approximately pH 3) in the presence of sodium lauryl sulfate is 2×10^{-2} $\sec^{-1}$ corresponding to a half-life with respect to rearrangement of 1,2-diphenylhydrazine of 35 seconds.

104.5 Data Summary

The information that was found about 1,2-diphenylhydrazine with regard to its aquatic fate is summarized in Table 104-1. 1,2-Diphenylhydrazine is in rapid redox equilibrium with azobenzene. Which compound of the pair that will be present in ambient waters depends upon the oxidation potential of the water. Well aerated surface waters will favor azobenzene while reducing conditions, that may occur in the bed sediment, will allow 1,2-diphenylhydrazine to predominate. Photoreduction or biodegradation may provide the only pathway to mineralization under contemporary environmental conditions. Sorption onto particulates is probably the main transport process for this pollutant, and, in the absence of a reasonably rapid biodegradation or photoreduction to aniline, sorption by the bed sediment as both 1,2-diphenylhydrazine and azobenzene could be the pollutant's short-term environmental fate.

Table 104-1

Summary of Aquatic Fate of 1,2-Diphenylhydrazine

Environmental Process[a]	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Although photoreduction to aniline is not expected to proceed rapidly, it may make a significant contribution to what may be the main pathway to ultimate destruction.	-	-	Medium
Oxidation	Oxidation to azobenzene is rapid and reversible; further oxidation of azobenzene itself probably does not occur under environmental conditions.	-	-	High
Hydrolysis	Not expected to occur under environmental conditions.	-	-	Medium
Volatilization	Not expected to be an important transport process.	-	-	Low
Sorption	Adsorption to particulates may provide sites for photoreduction; this is probably the main environmental transport and storage mechanism.	-	-	Medium
Bioaccumulation	Highly probable based on partition coefficients; no environmental data available.	-	-	Low
Biotransformation/ Biodegradation	Vertebrates transform this pollutant to aniline and benzidine; no environmental data available.	-	-	Low

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

104.6 Literature Cited

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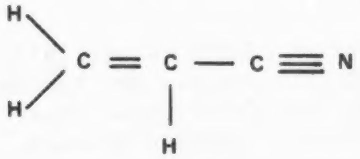
105. ACRYLONITRILE

105.1 Statement of Probable Fate

Although very limited information pertaining to the environmental fate of acrylonitrile was found in the reviewed literature, the volatility of this pollutant will ensure that a significant portion of it will be transported from the aquatic environment to the troposphere where it will undergo photooxidation. The acrylonitrile which remains in surface waters may be somewhat persistent but will be dissipated by dilution and current flow. Hydrolysis and sorption will probably not be important fate processes under most conditions. Bioaccumulation of acrylonitrile in aquatic organisms probably will not occur, but the cyanoethylation of proteins in aquatic biota is a distinct possibility. Acrylonitrile is degraded by sewage sludge, but no information was found regarding its biodegradability in natural surface waters.

105.2 Identification

Acrylonitrile has been detected in river water (Shackelford and Keith 1976). The chemical structure is shown below.



Acrylonitrile

Alternate Names

Vinyl cyanide
Cyanoethylene
Propenonitrile

CAS NO. 107-13-1
TSL NO. AT 52500

105.3 Physical Properties

The general physical properties of acrylonitrile are presented below.

Molecular weight (Windholz 1976)	53.06
Boiling point at 760 torr (Weast 1977)	78.5°C
Vapor pressure at 22.8°C (Weast 1977)	100 torr

Solubility in water at 20°C (Windholz 1976)	73,500 mg/l
Log octanol/water partition coefficient (Calc. by method of Leo et al. 1971)	-0.14

105.4 Summary of Aquatic Fate Data

105.4.1 Photolysis

Acrylonitrile does not exhibit significant absorption in the visible or near ultraviolet spectral regions; therefore, direct photolysis of this pollutant probably does not occur. Its system of conjugated double bonds, however, can accept electronic excitation energy via a photosensitizer (Bowman et al. 1974). Electronically excited acrylonitrile forms cyclobutane-type addition products with naphthalene and, therefore, probably could form similar compounds with some naturally occurring aromatic rings in the presence of photosensitizing plant pigments or industrially produced dyes. Such conditions might possibly obtain in highly polluted surface waters.

105.4.2 Oxidation

The calculated vapor pressure of 100 torr at 22.8°C (Weast 1977) indicates that volatilization will be a major transport process for the removal of this compound from water. Although it is very likely that this pollutant will be reprecipitated with water during the formation of rain, its expected rate of destruction in the troposphere probably makes atmospheric photooxidation a significant fate process. Organic molecules with unsaturated double bonds are the most reactive compounds that have been studied in simulated smog chambers (Altshuller et al. 1962; Laity et al. 1973). It has been extensively demonstrated that the mechanism for decomposition involves electrophilic attack by hydroxyl radical, ozone, or other oxidants on the double bond. Thus, reactivity generally decreases with substitution of electron-withdrawing groups on the carbon atoms of the double bond. Altshuller et al. (1962) have reported that the half-conversion time for the disappearance of ethylene and m-xylene, under the conditions employed for smog chamber studies, is approximately four hours. The decomposition of acrylonitrile should proceed somewhat more slowly due to the electron-withdrawing resonance and inductive effects of the cyano group attached to the double bond. The actual temporal stability of acrylonitrile under atmospheric conditions, however, cannot be directly extrapolated from these relationships because laboratory irradiation experiments are usually conducted for relatively short periods of time and do not account for all of the meteorological variables within an environmental airshed.

105.4.3 Hydrolysis

The hydrolysis of acrylonitrile to acrylamide or acrylic acid requires a strong acid mixture and elevated temperatures (American Cyanamid Company 1959) and, therefore, is probably not relevant to natural surface waters.

105.4.4 Volatilization

Although no information pertaining specifically to the volatilization of acrylonitrile was found in the reviewed literature, a vapor pressure of 100 torr at 22.8°C (Weast 1977) indicates that volatilization will be important in the transport of this pollutant from the aquatic environment into the atmosphere. Volatilization from water is dependent on a number of environmental factors (temperature, humidity, rate of water evaporation, mixing, and air currents) as well as the vapor pressure and solubility of the chemical. As an example from experiments with a compound structurally related to acrylonitrile, data developed by Dr. S.J. Broderius of the University of Minnesota-St. Paul (Broderius 1977) indicate that volatilization of hydrogen cyanide from water is a major transport process. In the laboratory, ten 8-liter samples of natural waters were spiked with hydrogen cyanide (25 to 200 μg/l) and exposed to the atmosphere. Volatilization was first order with respect to initial concentration, and half-lives of 22 to 111 hours were calculated at temperatures from 10 to 25°C. When the experiment was performed outdoors, so that the solutions were exposed to moderate winds, the rate of loss of hydrogen cyanide increased by a factor of 2 to 2.5. Thus, although hydrogen cyanide is miscible with water and also participates in hydrogen-bonding with the water, volatilization is still important in its transport from aquatic systems. Similarly, acrylonitrile, as a low molecular weight, volatile organic cyanide, should also be removed from aquatic systems by volatilization.

105.4.5 Sorption

Acrylonitrile is so strongly sorbed by clays under hypohydrous conditions that it cannot be removed under reduced pressure (Yamanaka et al. 1974). In aquatic systems, however, the water molecules that normally would be associated with the clay structure can be expected to prevent any significant amount of the pollutant from becoming bound to the clay in this manner. These chemisorptive interactions, however, may be sufficiently strong to transitorily provide heterogeneous acidic and basic reaction sites for an acrylonitrile molecule. Sanchez et al. (1972) report that chloro-and trichloroacetonitrile undergo hydrolysis within the interlayer space of montmorillonite with the formation of the corresponding amides. It is uncertain whether acrylonitrile will be similarly hydrolyzed.

The calculated log octanol/water partition coefficient (P = -0.14) indicates that acrylonitrile should not be preferentially partitioned between water and lipophilic materials. Therefore, it is unlikely that sorption will function as a storage or transport mechanism for this pollutant in natural surface waters.

105.4.6 Bioaccumulation

Although acrylonitrile, with a log octanol/water partition coefficient calculated as -0.14, would normally not be expected to accumulate in aquatic organisms, there is a possibility that it will react with the amino and sulfhydryl groups of biological proteins (Gut et al. 1975). Acrylonitrile, as a distinct molecule, would not be acumulating but would result in the accumulation of cyanoethylated proteins.

105.4.7 Biotransformation and Biodegradation

The biodegradation of acrylonitrile is reported to occur readily at concentrations less than 20 mg/l during anaerobic digestion processes operated in municipal sewage treatment facilities (Lank and Wallace 1970). Slave et al. (1973) observed that a *Pseudomonas*-containing sludge, used for the treatment of industrial acrylonitrile wastes, could degrade up to 35 percent of the pollutant at concentration levels of 500 mg/l. No information was found indicating that biodegradation of acrylonitrile would occur in natural surface waters.

The catabolism of acrylonitrile by terrestrial mammals has been investigated more thoroughly (Gut et al. 1975). Acrylonitrile is metabolized to thiocyanate which is then eliminated in the urine. Considerable species and organ difference in mammalian ability to detoxify acrylonitrile was observed.

105.4.8 Other Reactions

Cyanoethylation is the name for a group of addition reactions in which a polar molecule attacks the terminal carbon atom of the carbon-carbon double bond of acrylonitrile (Bruson 1949). In an aquatic environment, the reaction between water and acrylonitrile would lead to 3-hydroxypropionitrile and bis(2-cyanoethyl)ether. For the reaction to proceed significantly at ambient environmental temperatures, a basic catalyst would be required. Heterogeneous catalysis on clay surfaces is a reasonable possibility.

Treatment of acrylonitrile with chlorine-water or a solution of sodium hypochlorite leads to the formation of 2-chloro-3-hydroxypropionitrile (Bruson 1949). The reaction conditions are essentially those that would be met during chlorine-disinfection procedures in a water treatment facility.

105.5 Data Summary

The available information on the aquatic fate of acrylonitrile is summarized in Table 105-1. A significant portion of the acrylonitrile in aquatic environments will be transported to the troposphere where it will undergo photodegradation. The acrylonitrile which remains in natural surface waters will probably be characteristically persistent. Sewage sludge biodegrades acrylonitrile but there may be an insufficient population of microorganisms in the water column and insufficient contact time for biodegradation to be effective in surface waters. Hydrolysis, sorption, and bioaccumulation are probably unimportant under most conditions. Cyanoethylation of proteins in aquatic organisms exposed to acrylonitrile is a possible pollutant-biota interaction.

Table 105-1

Summary of Aquatic Fate of Acrylonitrile

Environmental Process[a]	Summary Statement	Rate	Half-Life ($t_{1/2}$)	Confidence of Data
Photolysis	Direct photolysis is improbable in aquatic environments.	-	-	Low
Oxidation	Photooxidation in the troposphere is a major fate process.	-	~4 hours	Medium
Hydrolysis	Not environmentally significant.	-	-	Medium
Volatilization	Most likely major transport process.	-	-	Medium
Sorption	Adsorption on organic sediment is improbable; transitory adsorption on clay is possible but not experimentally substantiated in aquatic systems.	-	-	Low
Bioaccumulation	Bioaccumulation as acrylonitrile itself is improbable; cyanoethylation of proteins is a possibility.	-	-	Low
Biotransformation/ Biodegradation	Degraded by sewage sludge; no information available on natural surface waters.	-	-	Low

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a. There is insufficient information in the reviewed literature to permit assessment of a most probable fate.

105.6 Literature Cited

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